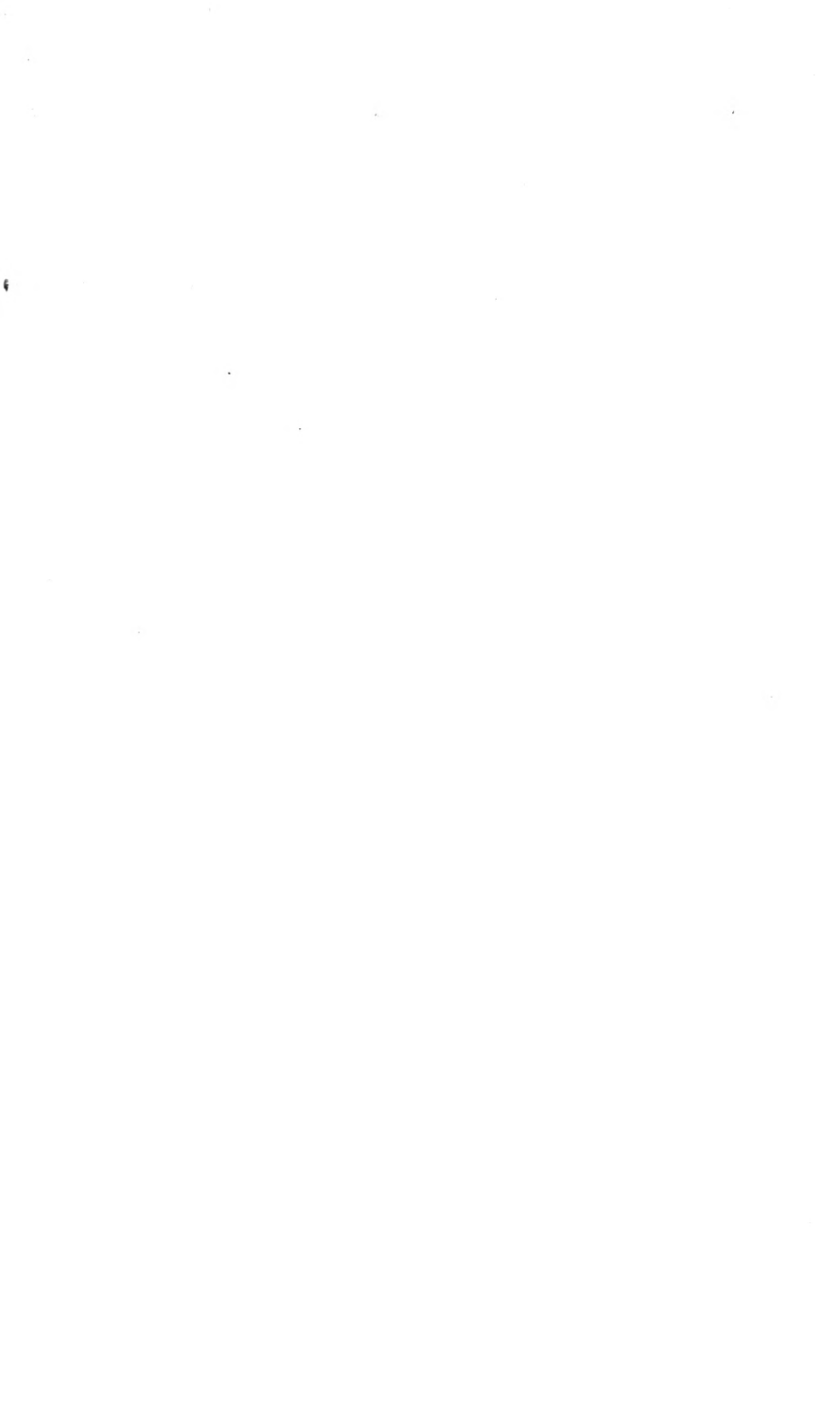# AMERICAN

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ON THE ACTION OF ALDEHYDES AND AMMONIA ON BENZIL.[1]

By Francis R. Japp and Samuel C. Hooker.

In former communications,[2] relating to the joint action of aldehydes and ammonia on compounds containing the dicarbonyl-group ($-CO-CO-$), two general reactions of this class have been described:

$$\text{I.} \quad \begin{array}{c} X'-CO \\ | \\ X'-CO \end{array} + R'-CHO+NH_3 = \begin{array}{c} X'-C-O \\ \| \\ X'-C-N \end{array}\!\!\!\diagdown\!\!\!\diagup C-R'+2OH_2.$$

and

$$\text{II.} \quad \begin{array}{c} X'-CO \\ | \\ X'-CO \end{array} + R'-CHO+2NH_3 = \begin{array}{c} X'-C-NH \\ \| \\ X'-C-N \end{array}\!\!\!\diagdown\!\!\!\diagup C-R'+3OH_2.$$
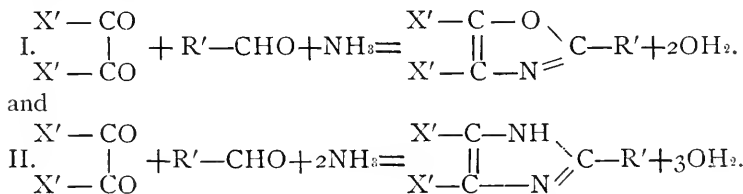
In addition to the above, it was mentioned (Chem. Soc. Journal, 1883, Trans. 17) that with certain aldehydes a third and totally distinct reaction occurs. Thus benzil, salicylaldehyde, and ammonia react according to the equation—

$$\underset{\text{Benzil.}}{C_{14}H_{10}O_2} + \underset{\substack{\text{Salicyl-}\\\text{aldehyde.}}}{2C_7H_6O_2} + 2NH_3 = \underset{\substack{\text{New}\\\text{compound.}}}{C_{28}H_{24}N_2O_4} + 2OH_2.$$
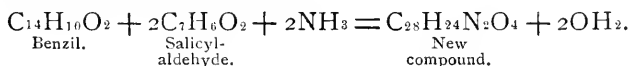
A precisely similar reaction occurs when furfuraldehyde is substituted for salicylaldehyde.

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[1] Communicated by the authors.

[2] Chem. Soc. Journ. Trans. 1880, p. 666; 1881, p. 225; 1882, pp. 146, 157 and 323; 1883, pp. 9 and 197.

The present communication is devoted to an account of this new reaction, and to a study of the compound obtained with salicylaldehyde. We venture to think that we have succeeded in throwing light on the constitution of this compound. The general reaction, corresponding with that in which the compound is formed, may be expressed by the following equation:

$$\text{III.} \quad \begin{matrix} X'\text{—CO} \\ | \\ X'\text{—CO} \end{matrix} + 2R'\text{—CHO} + 2NH_3 = \begin{matrix} R'\text{—CH—NH—CO—X'} \\ | \\ R'\text{—CH—NH—CO—X'} \end{matrix} \\ + 2OH_2.$$
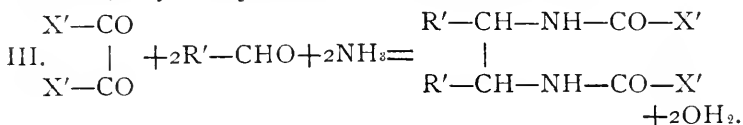
This reaction differs from the two foregoing in the fact that whereas in these the two carbon-atoms of the dicarbonyl-group become doubly linked, in the present reaction, as we shall endeavor to show, the atoms undergo separation, so that the diketone is broken up in two halves, which become two substituting acid radicals in the molecule of the new compound; and at the same time the two aldehyde residues become linked by means of the carbon-atoms of the CHO-groups.

In the first two reactions the aldehyde is oxidised at the expense of the diketone; in the third the reverse is the case, and the diketone is oxidised at the expense of the aldehyde. Thus, in the hydrolytic decomposition of the compounds formed in equations I and II, the aldehyde part of the molecule is eliminated as the corresponding acid; in the decomposition of the compounds formed in equation III, the diketone residues are liberated as two molecules of an acid having the same radical as the diketone.

The salicylaldehyde compound was selected for study, partly because of the ease with which it could be prepared, but chiefly on account of the readiness with which the various compounds obtained in its decomposition could be identified. According as a salicylic or a benzoic derivative was obtained in any given decomposition of the compound, there was the certainty that the percentage of that portion of the molecule must be ascribed to the aldehyde on the one hand, or to the diketone on the other.

Action of Salicylaldehyde and Ammonia on Benzil.

Equal weights of salicylaldehyde and benzil were dissolved in alcohol with the aid of heat, and the warm solution was saturated with gaseous ammonia. During the process the new compound

separated as a lemon-yellow crystalline powder. In order to prevent the delivery-tube from being choked by the solid substance, the ammonia was passed into the liquid through a wide T-piece, one end of the cross-limb of which was closed by a perforated cork, whilst the other was immersed in the liquid. A glass rod, working air-tight through the cork, served to clear the tube without interrupting the operation.

The saturated liquid was allowed to stand for some hours, after which the substance was filtered off and extracted two or three times with boiling alcohol, in which it is practically insoluble. In this condition it was employed for the various reactions about to be described, although it still retained its yellow color. The yield in various operations was very constant, and amounted to about three-fourths of the united weights of the benzil and salicylaldehyde employed.

For analysis a portion was further purified by dissolving it in boiling phenol and precipitating with alcohol, repeating these operations. It was thus obtained as a white crystalline sandy powder, consisting of microscopic plates. When heated in a capillary tube it becomes dark-colored at about 260°, and fuses with decomposition above 300°. It is almost insoluble in alcohol, ether, glacial acetic acid, and the other ordinary organic solvents. Boiling phenol dissolves it most readily.

Analysis gave figures agreeing with the formula $C_{28}H_{24}N_2O_4$.

	Substance.	CO_2.	OH_2.
I.	0.1190	0.3237	0.0582
II.	0.1678	0.4550	0.0844

III. 0.1140 gram burnt with copper oxide in a vacuum gave 6.1 cc. moist nitrogen at 14° and under 761 mm. pressure.

	Calculated for $C_{28}H_{24}N_2O_4$.		Found.		
			I.	II.	III.
C_{28}	336	74.34	74.19	73.95	...
H_{24}	24	5.31	5.43	5.59	...
N_2	28	6.19	...	...	6.30
O_4	64	14.16	...	...	...
	452	100.000			

The equation according to which this compound is formed has already been given.

It is remarkable that in the case of parahydroxybenzaldehyde the reaction with benzil ammonia takes place according to equation II, yielding parahydroxylophine,[1] whereas, when the isomeric salicylaldehyde is substituted for the para-compound, the reaction takes place as above according to equation III.

Action of Caustic Soda on the Condensation Product.—The compound dissolves in caustic soda. The solution was boiled for several days, at the end of which time nearly the whole of the substance was precipitated unchanged on the addition of hydrochloric acid. Some slight decomposition had, however, taken place, as a small quantity of benzoic acid could be extracted from the acidified liquid by treatment with ether, but no salicylic acid could be detected.

By fusion with caustic soda the substance yields benzoic and salicylic acids. The former was identified by its fusion point, the latter by the violet coloration with ferric chloride.

Action of Hydrochloric Acid on the Condensation Product.— By heating the compound with dilute hydrochloric acid (fuming acid diluted with twice its volume of water) at a temperature of 210° in sealed tubes for five hours, the benzil portion of the molecule is removed as benzoic acid and the hydrochloride of a new base is obtained. When a more concentrated acid or a higher temperature is employed, the benzoic acid is obtained as before, but the base is resinised, whilst at a somewhat lower temperature no action takes place. A large excess of the aqueous acid must be used, as any substance which is not in solution during the reaction is resinised. Even under the most favorable conditions it was found impossible to prevent entirely the formation of resin.

On warming the liquid thus obtained, the benzoic acid and the hydrochloride went into solution, whilst the resin, together with any unaltered substance, remained undissolved. The base, precipitated from the filtered solution by the addition of ammonia, was contaminated with resin. It was dissolved in an excess of hot benzene, and on cooling the liquid deposited the greater part of the resin. The filtered solution, which was only slightly colored, was evaporated to a small bulk, and, on cooling, yielded the base in a crystalline form. The substance was recrystallised from benzene until the constant fusing point 180.5° was obtained. It is readily soluble in hot benzene, almost insoluble in the cold. It is

[1] Chem. Soc. Jour. 1882, **1**, 326.

deposited from the benzene solution in groups of small lustrous laminæ, which are soluble in alcohol, ether and chloroform. Water dissolves it very slightly, but it is soluble in caustic alkalis.

Analysis gave numbers pointing to the formula $C_{14}H_{16}N_2O_2$.

	Substance.	CO_2.	OH_2.
I.	0.1282	0.3229	0.0764
II.	0.1226	0.3084	0.0735

III. 0.0991 gram burnt with copper oxide in a vacuum gave 10.05 cc. moist nitrogen at 20.3° and under 762.8 mm. pressure.

	\multicolumn{2}{c}{Calculated for $C_{14}H_{16}N_2O_2$.}		Found.	
			I.	II.	III.
C_{14}	168	68.85	68.69	68.60	...
H_{16}	16	6.56	6.62	6.66	...
N_2	28	11.48	...	...	11.62
O_2	32	13.11	...	...	...
	244	100.00			

This base is formed from the original compound according to the equation—

$$C_{28}H_{24}N_2O_4 + 2OH_2 = \underset{\text{Base.}}{C_{14}H_{16}N_2O_2} + \underset{\text{Benzoic acid.}}{2C_7H_6O_2}.$$
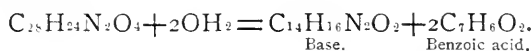
We shall show later that the original condensation product is a dibenzoyl-derivative of this base.

The preparation of any considerable quantity of the base by the foregoing method is a matter of great difficulty, but farther on a method will be described by which the base can be obtained with relative ease. The salts were prepared from a specimen of base obtained by this second method.

The *platinichloride* is deposited in large transparent orange-colored crystals, consisting of thick rhomboidal plates with bevelled edges, when platinic chloride is added in excess to a solution of the hydrochloride and the liquid is evaporated over sulphuric acid. The presence of an excess of hydrochloric acid is to be avoided, as it causes the salt to be contaminated with hydrochloride, which is less soluble in the concentrated acid than the platinichloride. The crystals contain water of crystallisation. They are permanent in air, but effloresce over sulphuric acid and become anhydrous at 100°.

0.5026 gram crystallised salt lost on heating to 100° 0.0501 gram.

Calculated for
$C_{14}H_{16}N_2O_2, 2HClPt, Cl_4, 4OH_2$ Found.

Water in 100 parts   9.89   9.97

0.2134 gram anhydrous salt left on ignition 0.0638 gram platinum.

Calculated for
$C_{14}H_{16}N_2O_2, 2HCl, PtCl_4$.   Found.

Pt in 100 parts   30.03   29.90

The *hydrochloride* is obtained as a crystalline powder, consisting of microscopic plates, when concentrated hydrochloric acid is added to a saturated solution of the base in dilute hydrochloric acid. It has a pungent, bitter taste, perceptible even with very dilute solutions.

The normal *sulphate* crystallises in prisms, very soluble both in water and in alcohol.

The *picrate* is precipitated in microscopic needles when an aqueous solution of picric acid is added to the solution of a salt of the base. It is practically insoluble in cold water, and dissolves only very slightly on boiling.

When fused with caustic soda the base yields salicylic acid as sole organic product.

As regards the constitution of this base, it is evident from its mode of formation (see equation) that it contains the whole of the salicylic portion of the molecule of the original compound. It therefore contains the group $(C.C_6H_4.OH)'''$ twice, and may be formulated $(C.C_6H_4.OH)_2N_2H_6$. It is very improbable that in the processes in which this compound has been formed a union of the nitrogen-atoms with each other can have occurred ; and the only alternative is to assume a union of the salicylic complexes, in which case the compound would have the formula—

$$C_6H_4(OH).CH.NH_2$$
$$|$$
$$C_6H_4(OH).CH.NH_2.$$
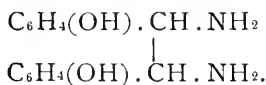
A compound of this constitution might be designated *dihydroxy-stilbenodiamine*, a name constructed on the analogy of *ethylene-diamine*.

The above formula accounts for the diacid character of the base, for its solubility in caustic alkalis, for the fact that it yields salicylic acid by fusion with caustic soda, and for the formation of the various compounds described farther on.

We sought for confirmation of this constitution in the action of nitrous acid on the compound. On adding a dilute solution of sodic nitrate to an acidulated solution of the base, gas was evolved and a neutral body separated, which, by crystallisation from benzene, was obtained in colorless microscopic octohedra. The quantity was unfortunately too small for further examination, the greater part of the base being resinised in the process. The failure was possibly due to the presence of the hydroxyl-groups ; by the action of hydriodic acid, however, it may be possible to convert the base into the non-hydroxylated compound, stilbene-diamine, and this with nitrous acid may possibly yield hydrobenzoin, thus definitively proving the constitution of the compound. These reactions will be studied by one of us as soon as the base has been obtained in sufficient quantity.

A systematic study of the reactions of the base, as compared with those of the orthodiamines of the benzene series, will also be undertaken. The base, as containing two amido-groups attached to contiguous carbon-atoms of a fatty chain, is a fatty analogue of an orthodiamine. It will be of special interest to ascertain whether the characteristic condensations in the ortho-series, of diamines with acids, aldehydes, etc., occur in the case of this compound. The analogy between benzene compounds of the ortho-series and certain fatty compounds, an analogy exemplified in the case of the phthalic and succinic compounds, of phthalide and the γ-lactones, of the anhydro-bases and glyoxaline, and in many other cases, points to a possibility of the occurrence of such reactions.

Action of Acetic Anhydride on the Condensation Product.—A quantity of the condensation product was boiled with twice its weight of acetic anhydride until the whole had dissolved, a process which required about six hours for completion. As soon as this happens, the boiling must be interrupted, since by the continued action of the anhydride the derivative first produced undergoes a further transformation, yielding a compound to be described further on. On cooling, the new substance separated from the dark solution in colorless rhomboidal laminæ. These were washed with alcohol and recrystallised from boiling acetic acid, from which they were deposited in the foregoing forms. The substance melted at 225–227°. The melting point was not altered by further recrystallisation. This compound is only sparingly soluble in boiling alcohol, separating in thin rhomboidal lustrous laminæ.

Analysis gave figures pointing to a diacetyl-derivative,

$$C_{28}H_{22}(C_2H_3O)_2N_2O_4.$$

	Substance.	CO_2.	OH_2.
I.	0.1120	0.2929	0.0527
II.	0.1258	0.3288	0.0601

III. 0.1776 gram burnt with copper oxide in a vacuum gave 8.35 cc. moist nitrogen at 23.5° and under 759.5 mm. pressure.

	Calculated for $C_{28}H_{22}(C_2H_3O)_2N_2O_4$.		Found.		
			I.	II.	III.
C_{32}	384	71.64	71.32	71.28	...
H_{28}	28	5.22	5.23	5.31	...
N_2	28	5.22	...	...	5.28
O_6	96	17.92	...	...	...
	536	100.00			

Hot dilute caustic potash dissolved the compound, at the same time removing the acetyl-groups; hydrochloric acid added to this solution precipitated the original condensation product.

The acetic anhydride mother-liquor from the diacetyl-derivative contained benzoic acid (or benzoic anhydride) derived from the decomposition of a portion of the substance, and also a mixture of compounds sparingly soluble in alcohol. We could not succeed in separating these last from one another. By long boiling with acetic anhydride they are converted into the compound described in the following paragraph.

By continuing the boiling of the condensation product with acetic anhydride for about eight hours after the whole of the substance had passed into solution, a totally different compound was obtained. On cooling, the dark-colored liquid deposited a crystalline substance, which was washed with acetic acid and then recrystallised from this solvent until the melting point remained constant. It was thus obtained in thin colorless prismatic crystals containing acetic acid. After expelling the acetic acid by heating at 130° the compound melted at 216–219°. The yield was about two-fifths of the weight of the condensation product taken. Analysis of the substance dried at 130° gave figures agreeing with the formula $C_{22}H_{24}N_2O_6$.

	Substance.	CO_2.	OH_2.
I.	0.1391	0.3254	0.0757
II.	0.1223	0.2855	0.0647

III. 0.1338 gram burnt with copper oxide in a vacuum gave 8.76 cc. moist nitrogen at 28.7° and under 755 mm. pressure.

	Calculated for $C_{22}H_{24}N_2O_6$.		Found.		
			I.	II.	III.
C_{22}	264	64.08	63.80	63.67	...
H_{24}	24	5.82	6.05	5.88	...
N_2	28	6.80	...	...	7.10
O_6	96	23.30	...	...	...
	412	100.00			

The compound dissolves readily in hot alcohol, and, on cooling, is deposited in thin colorless prisms containing 1 mol. of alcohol of crystallisation.

1.5322 grams of the substance, crystallised from alcohol and air-dried, lost on heating at 120° 0.1496 gram.

	Calculated for $C_{22}H_{24}N_2O_6$, C_2H_6O.	Found.
Alcohol in 100 parts,	10.04	9.76

We further satisfied ourselves that the compound $C_{22}H_{24}N_2O_3$ is formed from the pure diacetyl compound by long boiling with acetic anhydride. It may also be readily obtained by heating the original condensation product with acetic anhydride in a sealed tube at 150° for about four hours. At this higher temperature the transformation is very complete.

The acetic anhydride mother-liquor, which remained after the separation of the compound $C_{22}H_{24}N_2O_6$, contains large quantities of benzoic acid (or benzoic anhydride). After expelling the excess of acetic anhydride, the residue dissolved almost completely in boiling sodic carbonate, and, on adding hydrochloric acid, the benzoic acid was precipitated. It was identified by its fusing point and other characteristic properties.

The formation of the compound $C_{22}H_{24}N_2O_6$ from the original condensation product may be accounted for as follows : In the first place the diacetyl-derivative is formed ; this is then further acted on by acetic anhydride according to the equation—

$$C_{25}H_{22}(C_2H_3O)N_2O_4 + \begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}{>}O = C_{22}H_{24}N_2O_6 + \begin{matrix}C_6H_5.CO\\C_6H_5.CO\end{matrix}{>}O.$$

<div align="center">Diacetyl-   Acetic   Second   Benzoic
derivative.   anhydride.   acetyl-derivative.   anhydride.</div>
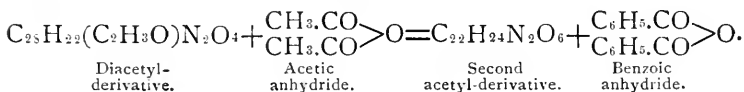
The simplest interpretation of this reaction would be that two benzoyl-groups in the diacetyl-derivative have been replaced by two acetyl-groups. If we, therefore, formulate the compound $C_{22}H_{24}N_2O_6$ as a tetracetyl compound, thus:

$$C_{14}H_{12}(C_2H_3O)_4N_2O_2,$$

it appears as a tetracetyl-derivative of a compound $C_{14}H_{16}N_2O_2$. This is, however, the formula of *dihydroxystilbenediamine*. The reactions of the compound $C_{22}H_{24}N_2O_6$, which we are about to describe, show it to be *diacetyl-diacetoxystilbenediamine :*

$$C_6H_4(O.C_2H_3O).CH.NH(C_2H_3O)$$
$$|$$
$$C_6H_3(O.C_2H_3O).CH.NH(C_2H_3O).$$
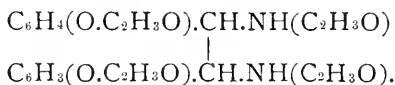
As, according to the above view, the whole of the benzil portion of the original molecule has been removed in the formation of this compound, it appeared important to show that no benzoic acid is obtained from the compound by oxidation. A portion was heated with potassium permanganate in akaline solution as long as the color of the permanganate was discharged. Not a trace of benzoic acid was obtained. The diacetyl-derivative of the condensation product, treated in the same way, yielded large quantities of benzoic acid.

Action of Caustic Alkali on the Compound $C_{22}H_{24}N_2O_6$.— 8 grams of the compound were boiled for a few minutes with a solution of 15 grams of potash in 75 cc. of water; it readily dissolved, and, on adding hydrochloric acid, a white substance was precipitated. This was filtered off, washed with water, boiled with alcohol, in which it is practically insoluble, and, after drying, was dissolved in hot phenol, and precipitated from the solution with alcohol. The crystallisation from phenol was repeated. In this way the substance was obtained as a white crystalline powder melting above 300°.

Analysis gave figures agreeing with the formula $C_{18}H_{20}N_2O_4$.

	Substance.	CO_2.	OH_2.
I.	0.1262	0.3042	0.0714
II.	0.1353	0.3263	0.0755

III. 0.1462 gram burnt with copper oxide in a vacuum gave 10.3 cc. moist nitrogen at 19° and under 768.8 mm. pressure.

	Calculated for $C_{18}H_{20}N_2O_4$.		Found.		
			I.	II.	III.
C_{18}	216	65.85	65.74	65.78	...
H_{20}	20	6.10	6.29	6.20	...
N_2	28	8.54	...	...	8.19
O_4	64	19.51	...	...	...
	328	100.00			

The action of the potash had, therefore, been to remove two acetyl-groups. These must be the two acetyl-groups attached to oxygen, as their removal constitutes the condition of the solubility of the compound in alkalis. The new compound would thus be *diacetyldihydroxystilbenediamine*, and would possess the constitution—

$$C_6H_4(OH).CH.NH(C_2H_3O)$$
$$|$$
$$C_6H_4(OH).CH.NH(C_2H_3O).$$
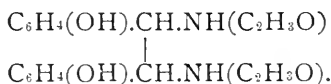
We show later on that the original condensation-product, which in its physical properties (high fusing point, sparing solubility, etc.) closely resembles the present compound, is the corresponding dibenzoyl-derivative of the base—*dibenzoyldihydroxystilbenediamine*.

By boiling the compound $C_{22}H_{24}N_2O_6$ with strong potash for an hour, all four acetyl-groups were removed, and the base dihydroxystilbenediamine was formed. This was separated by acidifying the solution with hydrochloric acid and then precipitating with ammonia. A considerable quantity of resin was formed by the action of the strong potash, which rendered the purification of the base a matter of difficulty. For this reason the melting point was found too low—$175°$ instead of $180.5°$. A microscopic examination of the crystals showed that they had exactly the same forms as those of the base already described. All doubt as to the identity of the two products is dispelled by the result of the action of hydrochloric acid on the compound $C_{22}H_{24}N_2O_6$, a reaction in which the base can readily be obtained in a state of purity.

Action of Hydrochloric Acid on the Compound $C_{22}H_{24}N_2O_6$.— Fuming hydrochloric acid dissolved the compound in the cold. On standing, and more rapidly on heating, the solution deposited a white crystalline substance. The physical properties of this pointed to its identity with diacetyldihydroxystilbenediamine, the compound obtained by the foregoing action of dilute potash. The

substance, after being dissolved in phenol and precipitated with alcohol, yielded on analysis figures agreeing with the required formula $C_{18}H_{20}N_2O_4$. (Percentages: calculated, $C = 65.85$, $H = 6.09$; found, $C = 65.66$, $H = 6.23$.)

By heating the compound $C_{22}H_{24}N_2O_6$ for three hours with concentrated hydrochloric acid in sealed tubes at 120°, the four acetyl-groups were removed and dihydroxystilbenediamine was obtained. On cooling, the tube contained large crystals of the hydrochloride. This method of preparing the base gives much better results than the direct decomposition of the original condensation compound with hydrochloric acid. In practice the compound $C_{22}H_{24}N_2O_6$ yields about half its weight of pure base. The base, liberated from the hydrochloride by ammonia, was purified as before by crystallisation from benzene.

The material employed in the various experiments, and in the preparation of the salts of the base, was prepared by the foregoing method.

Action of Benzoic Anhydride on the Condensation Product.—A quantity of the compound was heated with excess of benzoic anhydride until the whole had liquefied. The cooled product of the reaction was treated with alcohol, to remove benzoic anhydride and benzoic acid. The undissolved portion was recrystallised from acetic acid, and was thus obtained in colorless microscopic plates, which melted at 246–248°.

Analysis gave figures agreeing with the formula of a dibenzoyl-derivative, $C_{28}H_{22}(C_7H_5O)_2N_2O_4$:

	Substance.	CO_2.	OH_2.
I.	0.1656	0.4607	0.0734
II.	0.1490	0.4151	0.0664

III. 0.1882 gram burnt with copper oxide in a vacuum gave 7.1 cc. moist nitrogen at 22.7° and 765.5 mm. pressure.

	Calculated for $C_{28}H_{22}(C_7H_5O)_2N_2O_4$.		Found.		
			I.	II.	III.
C_{42}	504	76.36	75.87	75.98	…
H_{32}	32	4.85	4:92	4.95	…
N_2	28	4.24	…	…	4.29
O_6	96	14.55	…	…	…
	660	100.00			

As it was important, from the point of view of the proof of the constitution of the condensation product which we are about to give, to show that no rearrangement of the atoms of the original molecule had taken place during the formation of this dibenzoyl-derivative, beyond the introduction of the benzoyl-groups, we converted this derivative back into the condensation product. This was accomplished by boiling the compound with dilute caustic potash (1 part of caustic potash dissolved in 8 parts of water) until nearly the whole had passed into solution, a process which required several hours. From the filtered liquid, hydrochloric acid precipitated a white substance, which, after crystallisation from phenol, had all the physical properties of the original condensation product, and yielded on analysis figures agreeing with the required formula, $C_{25}H_{24}N_2O_4$. (Percentages : calculated, $C = 74.33$, $H = 5.31$; found, $C = 74.54$, $H = 5.49$.)

Action of Acetic and Benzoic Anhydrides on Dihydroxystilbenediamine.—In the foregoing pages we have regarded the original condensation product, and a number of the compounds obtained from it, as derived from the base dihydroxystilbenediamine by the replacement of hydrogen by acid radicals. The facts adduced in support of this view have been chiefly analytical.

The experiments about to be described furnish confirmatory evidence by the synthetic production of these compounds from the base.

A portion of the base was treated with acetic anhydride in the cold. A reaction immediately took place, with development of heat, and a very difficultly soluble white compound was formed, which by its physical properties was recognised as diacetyldihydroxystilbenediamine.

A fresh quantity of the base was heated in a sealed tube with acetic anhydride for several hours at 150°. In this way diacetyldiacetoxystilbenediamine was obtained. It was deposited from its hot alcoholic solution in the characteristic thin colorless prisms, which, after heating to expel the alcohol of crystallisation, melted at 216-219°.

A quantity of the base was heated with benzoic anhydride. At first the whole fused ; then, almost immediately, a difficultly fusible substance separated. This was in all probability the original condensation-product, which had thus been regenerated ; but, as the quantity of base at our disposal was limited, we preferred to

carry the reaction further and obtain the dibenzoyl-derivative of the condensation-product, which can be more readily purified than the condensation-product itself. The heating was, therefore, continued until the whole had again fused, after which the operation was interrupted. The product of the reaction was treated with alcohol, and the insoluble portion was crystallised from acetic acid. The compound was thus obtained in microscopic plates indistinguishable from those of the dibenzoyl-derivative of the condensation-product, and, like these, melting at 246–248°.

The dibenzoyl-derivative of the condensation-product,

$$C_{28}H_{22}(C_7H_5O_2)_2N_2O_4,$$

is, therefore, identical with the tetrabenzoyl-derivative of the base. It would thus have the formula—

$$C_6H_4(O.C_7H_5O).CH.NH(C_7H_5O)$$
$$|$$
$$C_6H_4(O.C_7H_5O).CH.NH(C_7H_5O).$$
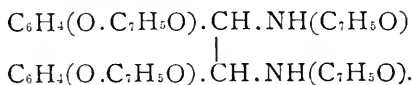
We have already shown that this compound may be converted into the condensation-product by boiling it with potash, two benzoyl-groups being removed in the process. Thus the synthesis of this product from the base has been accomplished. As the condensation-product is soluble in caustic alkalis, the two benzoyl-groups which are thus removed must be those which are attached to oxygen in the above compound. The condensation-product is, therefore, *dibenzoyldihydroxystilbenediamine*, and its formation from salicylaldehyde, benzil, and ammonia may be represented thus:

$$2C_6H_4(OH).CHO + \begin{matrix} CO.C_6H_5 \\ | \\ CO.C_6H_5 \end{matrix} + 2NH_3 =$$

$$\begin{matrix} C_6H_4(OH).CH.NH.CO.C_6H_5 \\ | \qquad\qquad\qquad | \\ C_6H_4(OH).CH.NH.CO.C_6H_5 \end{matrix} + 2OH_2.$$

Dibenzoyldihydroxystilbenediamine.
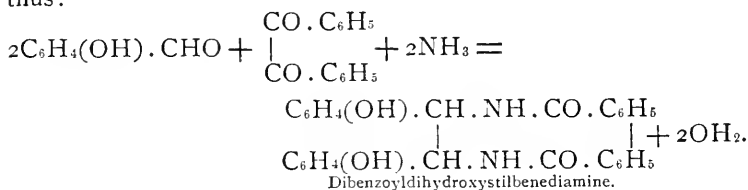
Action of Furfuraldehyde and Ammonia on Benzil.—20 grams of benzil together with 18 grams of furfuraldehyde were dissolved in alcohol, and the liquid was saturated with gaseous ammonia, conducting the operation as already described (pp. 2 and 3). At first a heavy granular white powder separated, but, when the saturation was nearly complete, the liquid became filled with a bulky substance,

differing in appearance from the first. After standing for some hours the mixture of substances was filtered off and boiled with alcohol, which dissolved only the bulky substance. The granular substance, which resembled in its properties the compound obtained with salicylaldehyde, was purified by dissolving it in hot phenol and precipitating with alcohol. It was deposited as a crystalline powder. It is practically insoluble in most of the ordinary solvents, but boiling glacial acetic dissolves it slightly. The melting point lies above 300°.

Analysis gave figures agreeing with the formula $C_{24}H_{20}N_2O_4$.

	Substance.	CO_2.	OH_2.
I.	0.1518	0.3989	0.0694
II.	0.1526	0.3301	0.0586

III. 0.1943 gram burnt with copper oxide in a vacuum gave 12.2 cc. moist nitrogen at 18.5° and under 757 mm. pressure.

	Calculated for $C_{24}H_{20}N_2O_4$.		Found.		
			I.	II.	III.
C_{24}	288	72.00	71.67	71.68	...
H_{20}	20	5.00	5.08	5.19	...
N_2	28	7.00	...	...	7.20
O_4	64	16.00	...	...	...
	400	100.00			

The following equation, which exactly corresponds with that in which the compound from salicylaldehyde is formed, expresses the reaction:

$$C_{14}H_{10}O_2 + 2C_5H_4O_2 + 2NH_3 = C_{24}H_2N_{20}O_4 + 2OH_2.$$

Benzil.　Furfuraldehyde.　New compound.
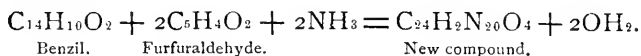
The second compound formed in the above process was purified by recrystallisation from alcohol until the melting point remained constant. It was deposited from its solution in boiling alcohol in tufts of silky needles melting at 246°. Analysis showed that this compound possessed the same percentage composition as the foregoing.

	Substance.	CO_2.	OH_2.
I.	0.1163	0.3061	0.0533

II. 0.1328 gram burnt with copper oxide in a vacuum gave 8.8 cc. moist nitrogen at 21.3° and under 752.5 mm. pressure.

| | Calculated for $C_{24}H_{20}N_2O_4$. | | Found. | |
			I.	II.
C_{24}	288	72.00	71.78	...
H_{20}	20	5.00	5.09	...
N_2	28	7.00	...	7.45
O_4	64	16.00	...	...
	400	100.00		

We have as yet made no experiments to ascertain the nature of this isomerism.

The study of these reactions, including those of dihydroxystil-benediamine already indicated, will be continued.

NORMAL SCHOOL OF SCIENCE,
    SOUTH KENSINGTON, LONDON.

ON CONDENSATION COMPOUNDS OF BENZIL WITH ETHYL ALCOHOL.[1]

BY MARY E. OWENS AND FRANCIS R. JAPP.

In preparing benzilic acid by heating benzil with alcohol potash, Jena[2] observed the formation of a neutral compound, melting at 200°, to which he ascribed the formula $C_{14}H_{12}O_2$, regarding it as isomeric with benzoïn. He assigned to it the name *tolane alcohol.* The quantity at his disposal was insufficient for further investigation.

Limpricht and Schwanert[3] obtained the same compound by heating together benzoïn and alcoholic potash with access of air. They arrive at the conclusion that it is a derivative of benzoïn (although they show in the same experiment that benzil is formed under the above conditions by the oxidising action of the air upon the benzoïn), and state their suspicion that the benzil employed by Jena must have contained benzoïn. On the strength of their analyses (not published) they arrive at the formula $C_{30}H_{26}O_4$, and name the compound *ethyldibenzoïn.*

We have found that, by the protracted action of very dilute alcoholic potash upon benzil in the cold, the above compound is

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[1] Communicated by the authors.   [2] Liebig's Annalen **155**, 79.
          [3] Ber. d. deutsch. chem. Ges. **4**, 335.

formed in large quantity. The yield, amounting in one experiment to 6 grams from 10 grams of carefully purified benzil, quite precludes the possibility of a formation from benzoïn present as an impurity. Our analyses lead to the formula $C_{30}H_{24}O_4$, which differs from that of Limpricht and Schwanert by containing two atoms of hydrogen fewer. The formation of such a compound from benzil and alcohol might be expressed by the equation

$$2C_{14}H_{10}O_2 + C_2H_6O = C_{30}H_{24}O_4 + OH_2.$$
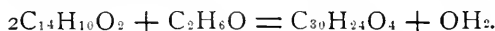
In order to prepare this compound, 10 grams of caustic potash were dissolved in $2\frac{1}{2}$ litres of alcohol, and to the solution thus obtained 200 grams of finely powdered benzil were added. The whole was shaken until the liquid was saturated with benzil, after which it was allowed to stand, shaking from time to time. The separation of the compound begins at the end of the first or second day, and is practically complete in about a fortnight. It is thus obtained as a crystalline powder, but when a larger quantity of alcohol is employed, so as to have all the benzil in solution from the commencement, it separates in moderately large lustrous crystals.

The crude substance was washed with ether to remove unaltered benzil, and then recrystallised, first from benzene, and afterwards from alcohol. The latter solvent deposits the compound in small lustrous crystals. These contain alcohol of crystallisation, which they lose only after long heating at 120°. At 100° they are permanent. The compound thus freed from alcohol melted at 200–201°, and yielded on analysis numbers agreeing with the formula $C_{30}H_{24}O_4$. We append, for the sake of comparison, the theory for Limpricht and Schwanert's formula $C_{30}H_{26}O_4$:

	Substance.	CO_2.	OH_2.
I.	0.1258	0.3694	0.0612
II.	0.1448	0.4260	0.0702

	Calculated for $C_{30}H_{24}O_4$. (Owens and Japp.)	Calculated for $C_{30}H_{26}O_4$. (Limpricht and Schwanert.)	Found. I.	Found. II.
C	80.36	80.00	80.08	80.24
H	5.36	5.78	5.41	5.38
O	14.28	14.22	...	...
	100.00	100.00		

The difference in the percentages required by the two formulæ is certainly rather small for analysis alone to decide between them,

but we think that the mode of formation which we have just
described renders the first formula the more probable.   Further,
if the second formula was correct, the errors of analysis, both for
carbon and hydrogen, would be in the wrong direction, whereas
with the first formula the errors are in the usual direction.

We think that the results obtained by our predecessors are
possibly due to their having overlooked the alcohol of crystal-
lisation, or, at all events, to their not having taken into account the
difficulty of completely expelling this alcohol.   They crystallised
the substance from alcohol, but none of them mention the presence
of alcohol of crystallisation.   Jena appears to have analysed a
compound from which only a portion of the alcohol had been
expelled.   Thus, the formula $C_{30}H_{24}O_4,C_2H_6O$ requires C 77.73
and H 6.07 per cent., whilst Jena finds C 78.7 and H 5.8 per
cent., or values intermediate between the foregoing and those
required for the formula $C_{30}H_{24}O_4$.   A similar, though smaller,
error may have lowered the carbon and raised the hydrogen in
Limpricht and Schwanert's analyses.   The melting point of the
substance analysed would probably afford no intimation of the
presence of the alcohol, for we have found that the crystals
containing alcohol do not, unless the temperature is rapidly raised
in determining the melting point, melt lower than those from which
the alcohol has been previously expelled.

A determination of alcohol of crystallisation was made, with the
following result :

1.3890 gram of crystallised substance lost on heating at 120°
0.1284 gram.

	Calculated for $C_{30}H_{24}O_4,C_2H_6O$.	Found.
Alcohol in 100 parts,	9.31	9.24

As the percentage of hydrogen in the compound $C_{30}H_{24}O_4,C_2H_6O$
differs from that of a compound of the formula $C_{30}H_{26}O_4,C_2H_6O$,
we analysed a specimen of the air-dried substance containing
alcohol of crystallisation :

Substance	CO_2.	OH_2.
0.1145	0.3256	0.0619

	\multicolumn{2}{c}{Calculated for $C_{30}H_{24}O_4, C_2H_6O$.}	Found.
C_{32}	384	77.73	77.55
H_{30}	30	6.07	6.01
O_5	80	16.20	...
	494	100.00	

The formula $C_{30}H_{26}O_4,C_2H_6O$, on the other hand, requires C 77.42 and H 6.45 per cent. The value obtained for hydrogen, coupled with that yielded by the compound dried at 120°, appears to us to afford strong evidence in favor of the formula with less hydrogen.

From a solution in hot benzene, the condensation-product is deposited in minute rhomboidal plates, generally grouped in rosettes, and containing benzene of crystallisation. The crystals effloresce when exposed to the air and become opaque. A portion of the crystallised substance, freed from adhering benzene by pressure between filter-paper and brief exposure to the air, lost, on heating at 120°, 14.96 per cent. of its weight. The formula $C_{30}H_{24}O_4,C_6H_6$ requires a loss of 14.83 per cent.

Limpricht and Schwanert[1] state that by heating "ethyldi-benzoïn" with acetyl chloride a monacetyl-derivative melting at 145° is obtained. We have been unable to confirm this result. The substance may be heated for an hour with acetyl chloride at 100° without undergoing change. Protracted heating, or a higher temperature, produces resination. We were equally unable to obtain an acetyl-derivative by boiling the substance with acetic anhydride. We have, however, made an observation which, we think, explains the supposed existence of a monacetyl-derivative. When the condensation-product is recrystallised several times from glacial acetic acid, the melting point sinks each time until a limit is reached, when a substance is obtained melting at about 130°. This limit may be reached in a single crystallisation, by boiling the compound for some hours with the acetic acid. The substance thus obtained is not an acetyl-derivative, but a compound of the condensation-product with acetic acid (or possibly with acetyl and hydroxyl). On exposure to the air, and more rapidly on heating, it parts with acetic acid; and its melting point lies anywhere between 130° and 200° (the melting point of the original substance), according to the amount of drying to which it has been subjected. It is possible that Limpricht and Schwanert, if they employed acetic acid as a solvent, may have obtained this molecular compound, and analysed a product from which the acetic acid had been only partially expelled. This would account for the melting point found by these investigators; and the substance in this condition would also give figures agreeing more or less closely with those required for a monacetyl-derivative, seeing that the composition of such a

[1] *Loc. cit.*

derivative lies almost intermediate between that of the molecular compound and that of the original condensation-product.

	Calculated for		
	$C_{30}H_{24}O_4,C_2H_4O_2$.	$C_{30}H_{23}(C_2H_3O)O_4$.	$C_{30}H_{24}O_4$.
C	75.59	78.37	80.36
H	5.51	5.31	5.36
O	18.90	16.32	14.28
	100.00	100.00	100.00

A specimen of the molecular compound, melting at 133°, gave on analysis C 75.48 and H 5.34 per cent.

As Limpricht and Schwanert publish no details of preparation, or analytical figures, in connection with their acetyl compound, we have no means of testing the correctness of the above supposition.

In the benzene mother-liquors remaining from the purification of the foregoing condensation-product we found a second substance, which was deposited in minute yellow crystals melting at 232°. A larger quantity of this substance was obtained from the original alcoholic potash mother-liquors (after removing the compound $C_{30}H_{24}O_4$) by acidifying with hydrochloric acid, distilling off the alcohol to a small bulk, and precipitating the organic substance by the addition of water. This precipitated substance was treated with alcohol, in order to remove benzoic acid and a soluble resin, and the crystalline residue was dissolved in hot phenol and reprecipitated with alcohol. By a repetition of this crystallisation from phenol, the substance was obtained as a yellow crystalline powder, melting as above at 232°. Analysis gave numbers agreeing with the formula $C_{46}H_{34}O_4$:

	Substance.	CO_2.	OH_2.
I.	0.1354	0.4204	0.0657
II.	0.1534	0.4769	0.0742
III.	0.1492	0.4640	0.0735

	Calculated for $C_{46}H_{34}O_4$.		Found.		
			I.	II.	III.
C_{46}	552	84.92	84.67	84.78	84.81
H_{34}	34	5.23	5.39	5.37	5.47
O_4	64	9.85	...	...	...
	650	100.00			

These analyses were made with different preparations.

The formation of a compound of the above formula from benzil and alcohol may be expressed by the following equation :

$$3C_{14}H_{10}O_2 + 2C_2H_6O = C_{46}H_{34}O_4 + 4OH_2.$$
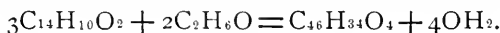
We have also found that dilute alcoholic potash acts slowly upon benzoïn in the cold, and, when air is excluded during the reaction, gradually converts it into a compound crystallising in silky needles, which melt at 250° and are apparently distinct from any of the compounds hitherto obtained by the action of potash upon benzoïn.   An account of this reaction is reserved for a future communication.

NORMAL SCHOOL OF SCIENCE,
    SOUTH KENSINGTON, LONDON.

ON A SCHEME FOR THE QUALITATIVE DETERMINATION OF THE BASES WITHOUT HYDROGEN SULPHIDE.

By George S. Eyster.

There are many technical laboratories fitted for special work where an extended qualitative examination is seldom made.   If a sulphuretted hydrogen apparatus is at hand it is out of order, and to put it in working condition often requires more time than the assay.   On the other hand, sulphydric acid solution keeps badly and is inconvenient to use from want of strength.   Strong solution of ammonium sulphide can now be had from the dealers in chemicals, and if preserved in a closet, its keeping powers are satisfactory.   It is much stronger than solution of sulphydric acid, and in many cases time can be saved by its use.

While the following scheme is not proposed as a complete substitute for the ordinary course of analysis in a well-equipped laboratory, yet from the experiments of the writer, he thinks its employment will, in most cases, be satisfactory to a careful analyst. It is intended especially for use in situations where hydrogen sulphide is not so available, and where, as in travelling, compactness in apparatus and materials is desirable.

The scheme is given in rather an extended shape, so that those who may wish to give it a trial will have all the main points at hand.   Zettnow's scheme has been followed to some extent in the use of sulphuric acid as a separating reagent.   Attention is called to some points, in the notes, that would not so readily occur to one accustomed only to the ordinary procedure.   It is hoped that the remaining precautions are such as would occur to any chemist. The old expressions, soda, potassa, ammonia (solution understood), are retained for brevity.

My thanks are due Prof. E. S. Breidenbaugh for facilities afforded me in the Chemical Laboratory of Pennsylvania College for the prosecution of necessary experiments in the testing of the following scheme.

Some of the rarer elements more likely to occur in ordinary work are merely indicated.

(The solution has a neutral or acid reaction.)

I. (Ag, Pb, Hg)

Add dilute hydrochloric acid, filter, wash. Precipitate 1, Filtrate II.

1. Wash with hot water, add H_2SO_4 to washings.   *White precipitate*, Lead.

2. Pour ammonia over residue from 1 ;

    a. Residue *blackens*, Mercury.

    b. Acidify filtrate from 1 with HNO_3.   *White precipitate*, Silver.

II.[1] (Ba, Sr, Ca, Pb)

Add dilute sulphuric acid.   Precipitate 1, Filtrate III.

1. Boil with sodium carbonate, filter, wash, dissolve in hydrochloric acid.

2[2]. Add ammonia and ammonia sulphide.   *Black precipitate*, Lead.

3[3]. Evaporate to dryness with HCl filtrate from 2, treat residue with strong alcohol, filter.   Examine Residue 4, Filtrate 5.

4. Test with flame reaction for *Barium*.

5. Add equal bulk water and a few drops hydrofluosilic acid, allow to stand, filter (Ba), add H_2SO_4, filter, wash with weak alcohol, boil with Na_2CO_3 and convert into chlorides (see 1 and 3),

add to solution potassium sulphate,[1] allow to stand. *White precipitate*, Strontium.

6. Add ammonia and oxalate of ammonium to filtrate from 5; allow to stand in warm place. *White precipitate*, Calcium.

III. (Hg, Pb, Bi, Cd, Cu, Co, Ni)

If the color indicates much *chromic acid*, boil with hydrochloric acid and a few drops alcohol until all the chromic acid is reduced, then, if enough HCl is not present, add NH_4Cl, and—

A. Add ammonia and ammonium sulphide, both in slight excess, heat, agitate, filter, wash. Precipitate *B*, Filtrate IV.

B[1]. Treat with ammonium sulphide in excess (if Cu be present, boil, or use sodium sulphide), filter, wash with water containing a little $(NH_4)_2S$. Residue *C*, Filtrate IV.

C. Treat with dilute HCl, filter, wash. Residue *D*, Filtrate V.

D. Boil with dilute HNO_3, filter, wash. Residue 1, Filtrate 2.

1. *Black residue*,[2] Mercury. *Test with* Na_2CO_3 *in glass tube.*

2[5]. Drive off excess acid, add dilute H_2SO_4. *White precipitate*, Lead.

3. To filtrate from 2 add ammonia. *White precipitate*, Bismuth.

4. Evaporate a small portion of the ammoniacal filtrate from 3 nearly to dryness, add a little acetic acid and potassium ferrocyanide. *Red precipitate* or *coloration*, Copper.

5. Precipitate remainder of filtrate from 3 by ammonium sulphide, boil resulting sulphides with dilute H_2SO_4, filter, wash. Residue 7, Filtrate 6.

6. Add ammonia (and if necessary $(NH_4)_2S$). *Yellow precipitate*, Cadmium.

7. Test a portion with borax bead for Ni, Co.

8. Dissolve remainder of precipitate in strong HCl, drive off excess acid, add potassium nitrite and acetic acid, allow to stand 12–24 hours in warm place. *Yellow precipitate*, Cobalt.

9. Add soda in excess. *Light green precipitate*, Nickel. [See note 6.]

IV₄. (As, Sb, Sn, Au, Pt) (Ni)

A. Add hydrochloric acid to the filtrate from III *A* in slight excess, filter, treat Filtrate VI. Treat filtrate from III *B* in the same manner and collect precipitate on the same filter (but the last

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[1] A *dilute* solution.　　　[2] Lead sulphate may also be present, and possibly Au, Pt, Sn.

filtrate is not saved), wash, dry, fuse with sodium carbonate and nitrate, treat with cold water, filter, wash with weak alcohol. Residue 1, Filtrate 5.

1. Heat with hydrochloric acid, add water, a piece of platinum and a fragment of C. P. zinc. When action ceases remove zinc, pour off liquid, warm residue with hydrochloric acid, test the solution with mercuric chloride. *White precipitate*, Tin.

2. Free residue from 1 from Sn by boiling with HCl and washing, warm in a dish, together with the piece of platinum employed in 1, with tartaric acid and water, and a few drops nitric acid added at the last, decant acid solution, test with ammonia and ammonium sulphide. *Orange precipitate*, Antimony.

3. Wash residue from 2, dissolve in aqua regia, evaporate, add ammonium chloride and weak alcohol. *Yellow precipitate*, Platinum.

4. Drive off alcohol from filtrate from 3, add solution ferrous sulphate. *Brown precipitate*, Gold.

5. Acidify with nitric acid, drive off CO_2, add ammonia and magnesia mixture. *White Crystalline precipitate*, Arsenic.

V. (Fe, Al, Cr, Zn, Mn [Ce, Ti])

Boil Filtrate III C, filter off S, add a few drops nitric acid, boil. Test a portion after cooling for Iron. If P is suspected and there is not enough Fe to combine, add Fe_2Cl_6 until a drop of the fluid gives a yellowish precipitate on a watch-glass with ammonia. In many cases, more especially in the absence of P, and where traces are not regarded, we can use the scheme A'.

A. Drive off excess of acid, add sodium carbonate until the fluid takes the deepest color it will assume without a precipitate, then milk of barium carbonate in slight excess, stir and allow to stand in the cold until the supernatant liquid is colorless; filter, wash. Precipitate 1, Filtrate 3.

A'. Add ammonia in *slight* excess (taking care that the fluid has enough ammonium chloride), heat to near boiling for some time, filter, wash. Precipitate 1, Filtrate 4.

1. Boil with soda, filter, add $(NH_4)Cl$, heat. *Precipitate*, Aluminum.

2. Fuse insoluble residue from 1 with Na_2CO_3 and $NaNO_3$, test for Chromium.

3. Acidify with HCl, boil, precipitate Ba by H_2SO_4. Proceed with filtrate 4.

4. Add ammonia and ammonium sulphide, filter, wash with water containing a little $(NH_4)_2S$. Examine filtrate for Ca and Mg; treat precipitate with acetic acid. Residue 5, Filtrate 7.

5. Treat with dilute HCl. Examine residue for Ni, Co. Filtrate 6.

6. Add nitric acid, concentrate, add soda, boil (if residue, test for Ni, Co if not yet found), filter, test filtrate with ammonium sulphide for Zinc.

7. Boil with soda, test precipitate with Na_2CO_3 for Manganese. [Dissolve a portion of the precipitate in A or A' in nitric acid, drive off excess NHO_3 and test with molybdic solution for phosphorus. If silica be present, remove before testing for phosphorus by evaporation to dryness.]

VI. (Ba, Sr, Ca, Mg [Li])

If Ba, Sr, Ca, have not been found, the filtrate IV A is now examined for small quantities of these bases by ammonium sulphate and oxalate in the usual manner; strontium and calcium sulphates can often be used to advantage in distinguishing Ba and Sr. Test a portion of the filtrate *completely* freed from Ba, Sr, Ca (by ammonium sulphate and oxalate and carbonate if necessary), with sodium phosphate for magnesia, treat remainder as in VII.

VII. (K, Na [Li])

Get rid of all other bases in the usual manner (Baryta water, or milk of lime, ammonium carbonate, ignition). Test for alkalies; with platinic chloride and alcohol for potassium; in filtrate, sodium as platinchloride (and with flame reaction).

NOTES.

It is hardly necessary to advise the testing for each section in a *small* portion of the liquid before proceeding with the main bulk of the solution.

II.

If a precipitate is not formed in the course of a few minutes, the analysis can be proceeded with. The course here laid down is often convenient, but the filtrate from NH_4OH and $(NH_4)_2S$ can be examined in the usual way with ammonium carbonate.

2.

2. Test a portion of the residue in 1 with $(NH_4)_2S$ on a watch-glass, and if Pb is not present, omit 2.

3.

3. Ignite if large quantities of ammonia salts are present.

III.

B. If Cu goes into the filtrate it may interfere to some extent with the detection of Sb. But with care Cu need not be confounded with Sb. If mercuric salts are present, sodium sulphide may give trouble by dissolving mercuric sulphide.

D. HCl and chlorides should be thoroughly washed out in the presence of mercuric salts.

5.

2. Be careful not to precipitate Bi by too great a dilution.

6.

9. In the presence of Cu, test for Ni with the S.Ph bead. If Cu be present, and no Ni, the bead will be green while hot and *blue* when cold. If Ni be present with Cu, the bead will be *green* when cold. If the analyst is not familiar with this test, several S.Ph beads containing varying amounts of Cu and no Ni should be made for comparison. The electrolytic separation may also be used.

IV.

The operator must not depend on the slight excess of $(NH_4)_2S$ dissolving the soluble sulphides, but should treat the first precipitate with a large excess, as indicated in the scheme.

The chemist is supposed to determine the degree of oxidation (or quantivalence) of the elements in the usual way.

VALUATION OF ACETATE OF LIME.

By A. A. Blair.

The wide variation in the results obtained by different methods for the valuation of acetate of calcium (pyrolignite of lime) led me to make the following investigations, which I hope may prove of interest. The distillation method with phosphoric acid is generally

considered the most accurate, but being very troublesome and tedious, is rarely used in commercial work. The carbonate of soda method is much more rapid, but is open to the objection that the solution of crude acetate of lime is so dark in color that it is extremely difficult to mark correctly the end reaction in the titration. Results obtained by calculating the amount of acetate from the lime determined by direct ignition are decidedly untrustworthy, owing to the fact that there is always an excess of base, and the results, consequently, are too high. It occurred to me that, if the solution of crude acetate could be readily decolorised, without changing the composition of the salt, the carbonate of soda method might be made extremely accurate. I therefore made the following experiments : I took a glass tube 50 cm. long and 17 mm. in diameter and closed the lower end with a rubber stopper, through which ran a small glass tube 76 mm. long and 5 mm. in diameter. On top of this stopper I placed a plug of fibrous asbestos 6 mm. thick, and then filled the tube three-quarters full of animal charcoal. Having secured this in a clamp, I filtered through it 5 grams of crude acetate of lime dissolved in 50 cc. of water, and washed it carefully. The solution came through perfectly colorless when the filtration was not too rapid. The rate of filtration is determined by the thickness of the asbestos plug, which can be easily regulated. When properly arranged, the filtration and washing require about two hours. A sample of good grey acetate distilled directly from phosphoric acid yielded as follows :

5 grams acetate, 50 cc. H_2O, 75 cc. H_3PO_4 distilled nearly dry ; 50 cc. H_2O added and distilled again ; 50 cc. added and distilled a third time. Distillate titrated with NaHO, using phenolphthalein as indicator, gave $Ca(C_2H_3O_2)_2$, 81.72 per cent.

A second determination made in the same way gave $Ca(C_2H_3O_2)_2$, 81.48 per cent.

Two determinations made by the carbonate of soda method, after filtering through animal charcoal, gave : 1st determination, $Ca(C_2H_3O_2)_2$, 81.89 per cent. 2d. determination, $Ca(C_2H_3O_2)_2$, 82.05 per cent.

Direct ignition and calculation from the amount of lime thus obtained gave $Ca(C_2H_3O_2)_2$, 86.02 per cent.

The residue, insoluble in water, was ignited and subtracted from the lime before calculating the latter to $Ca(C_2H_3O_2)_2$.

A second darker sample was taken and gave the following results:

Distilled direct.	Filtered through animal charcoal and distilled.	Na_2CO_3 method filtered through animal charcoal.	Direct ignition.
69.12 per cent.	69.29 per cent.	71.71 per cent.	73.05 per cent.
69.45	69.45	72.04	73.16

I then prepared some acetate of lime from C. P. acetic acid and pure $CaCO_3$, dried it carefully at 105° C. and obtained the following results:

Distilled direct.	Filtered through animal charcoal and distilled.	Na_2CO_3 method direct.
93.18 per cent.	93.49 per cent.	94.93 per cent.

Na_2CO_3 method filtered through animal charcoal.	Ignition.
95.01 per cent.	96.07 per cent.

Combustion of the acetate in chromate of lead and bichromate of potash gave, calculating the CO_2 obtained to $Ca(C_2H_3O_2)_2$, the H in the amount so calculated to H_2O, and the excess of H_2O, found by combustion over the calculated amount, as H_2O in the acetate:

$Ca(C_2H_3O_2)_2$.	H_2O.
92.50 per cent.	5.72 per cent.
92.50	5.83

Using the lime found by ignition, the acetic acid and water as determined by combustion, the composition of the acetate was—

Ca	24.32 per cent.
$(C_2H_3O_2)_2$	69.08
H_2O	5.83
	99.23

A sample of acetate of lime, prepared by filtering the crude pyrolignite through animal charcoal, acidulating with pure acetic acid, evaporating to dryness and drying at 105° C., gave me of $Ca(C_2H_3O_2)_2$—

Direct distillation.	Na_2CO_3 method.	Ignition.	Combustion.
90.01 per cent.	93.92 per cent.	94.49 per cent.	93.68 per cent.
90.25	93.87	...	...
90.25	93.87	...	...
...	93.87	...	...

The composition of the acetate, using the acetic acid obtained by combustion, the lime by ignition and the water by combustion, was—

Ca	.	.	.	.	.	23.92 per cent.
$(C_2H_3O_2)_2$	.	.	.	.	.	69.97
H_2O	.	.	.	.	.	6.55

100.44

All the samples, both of the crude and pure acetate, were alkaline to litmus, and both the pure samples contained, after long drying at 105° C., considerable water, besides an excess of lime over the amount necessary to form acetate of lime, although the first sample was alkaline at the start, and the second strongly acid with acetic acid.

The samples were all free from magnesia, phosphoric acid, hydrochloric acid, nitric acid and sulphuric acid.

It will be seen, by the comparative results obtained, that the composition of pyrolignite of lime is unaltered by filtering through animal charcoal, while the salt so filtered can be accurately valued by the carbonate of soda method.

The method of procedure I used is as follows:

Treat 5 grams of the pyrolignite with about 50 cc. water and filter through the tube containing animal charcoal as described above. The filtrate and washings should amount to about 250 cc. Heat to boiling in a beaker of about 500 cc. capacity, and add a weighed amount of Na_2CO_3 sufficient to precipitate all the lime as carbonate. Boil with constant stirring until the precipitate, at first floculent, becomes granular, then filter into a flask of about 1 L. capacity and wash thoroughly; add a measured excess of standardised sulphuric acid and boil for a few minutes to expel all CO_2. Cool, transfer to a white porcelain dish of about 1200 cc. capacity, add a few drops of phenolphthalein solution, and titrate with standard NaHO solution.

The method requires: 1. A standard solution of sulphuric acid. 2. A standard solution of caustic soda (to simplify calculation equal in strength to the sulphuric acid solution). 3. Dried Na_2CO_3 of known strength. 4. A solution of phenolphthalein. With the methods for preparing the solutions I give an actual example.

About 30 cc. concentrated C. P. H_2SO_4 to 1 L. water gave, as a means of several determinations by precipitating 20 cc. of the solution with an excess $BaCl_2$ solution,

1 cc. H_2SO_4 sol. $= .0508926$ gram H_2SO_4 log $= 8.7066546$
" " $= .0550470$ gram Na_2CO_3 log $= 8.7407344$.

NaHO *Solution.*

About 45 grams solid NaHO free from carbonate to 1 L. water gave a solution a little stronger than the H_2SO_4 sol., 20 cc. of the H_2SO_4 solution, diluted to about 1 L. and titrated in the dish after the addition of a few drops of the indicator, required 18 cc. of NaHO sol., then $18 : 20 = 1000 : 1111$; and by adding 111 cc. of water to the NaHO solution, the latter was reduced to exactly the strength of the H_2SO_4 sol., so that 1 cc. H_2SO_4 sol. $= 1$ cc. NaHO sol., as was found by a second titration.

Dried Na_2CO_3.

To determine the value of an impure carbonate of soda find value in H_2SO_4 sol., and consequent value in H_2SO_4; then $H_2SO_4 : Na_2CO_3$ $=$ value of imp. Na_2CO_3 in H_2SO_4 : value of imp. Na_2CO_3 in pure Na_2CO_3. Then multiply this factor by factor for reducing Na_2CO_3 to $Ca(C_2H_3O_2)_2$, and we have factor for reducing impure Na_2CO_3 to $Ca(C_2H_3O_2)_2$,

$$Na_2CO_3 : Ca(C_2H_3O_2)_2 = 1 : 1.4906 \; \log = 0.1733512.$$

1 gram of impure Na_2CO_3 (the sample I used contained a great deal of water), treated in a flask with 20 cc. H_2SO_4 sol. and boiled to expel CO_2, upon titration with NaHO sol. required 7.25 cc. NaHO sol. to neutralise it, then $20 - 7.25 = 12.75$ cc., and second experiment gave 7.35 cc.; $20 - 7.35 = 12.65$ cc.

The mean of 2 dets. $= 12.70$ cc.

1 gram $Na_2CO_3 = 12.70$ cc. H_2SO_4 sol.   Then

log value H_2SO_4 sol.	$= 8.7066546$
" 12.7	$= 1.1038037$
" value imp. Na_2CO_3 in H_2SO_4 sol.	$= 9.8104583$
" ratio $Na_2CO_3 : H_2SO_4$	$= 0.0340798$
" value imp. Na_2CO_3 in pure Na_2CO_3	$= 9.8445381$
" " pure Na_2CO_3 in $Ca(C_2H_3O_2)_2$	$= 0.1733512$
" " imp. Na_2CO_3 in $Ca(C_2H_9O_2)_2$	$= 0.0178893$

$$Na_2CO_3 = 106 \; \log = 2.0253059$$
$$H_2SO_4 = 98 \text{ " } = 1.9912261$$

$$\log \text{ ratio} = 0.0340798$$

Value of 1 cc. H_2SO_4 sol. in impure Na_2CO_3. 1 gram $= 12.7$ cc., or 1 cc. $= \frac{1}{12.7}$, or 1 cc. H_2SO_4 sol. $= 0.078741$ gram imp. Na_2CO_3 $\log = 8.8962009$.

Solution of Phenolphthalein.

Dissolve in alcohol and deliver the same number of drops from a small pipette for each titration. One drop of NaHO sol. suffices to change the yellow color of the acid solution to a bright and permanent pink.

Example of Valuation of Pyrolignite.

5 grams pyrolignite filtered, and sol. precipitated by 4 grams impure Na_2CO_3, 20 cc. H_2SO_4 sol. added, and when titrated with NaHO sol. it required 19.1 cc. to give the end reaction. Then $20 - 19.1 = 0.9$ cc. H_2SO_4, or the excess of impure Na_2CO_3, over and above the amount necessary to precipitate all the lime as carbonate, was equal to 0.9 cc. H_2SO_4 sol.

$$0.9 \qquad\qquad\qquad \log = 9.9542425$$
$$\text{Value 1 cc. } H_2SO_4 \text{ sol. in imp. } Na_2CO_3 \text{ `` } = 8.8962009$$
$$\overline{\qquad\qquad\qquad 18.8504434}$$

or the solution contained 0.07086 gram imp. Na_2CO_3, more than sufficient to precipitate the lime as carbonate. Subtracting this from the 4 grams added we leave 3.92914 grams imp. Na_2CO_3 as the amount necessary to neutralise the acetic acid in the pyrolignite. Then

$$3.92914 \qquad\qquad\qquad\qquad \log = 0.5942931$$
$$\text{Value of imp. } Na_2CO_3 \text{ in } Ca(C_2H_3O_2)_2 \text{ `` } = 0.0178893$$
$$4.0943 \text{ grams } Ca(C_2H_3O_2)_2 \qquad\qquad \text{`` } = 0.6121824$$

and dividing this by 5 we leave 0.8189 or 81.89 per cent. $Ca(C_2H_3O_2)_2$ in the pyrolignite.

NOTES ON THE ABSORPTION SPECTRUM OF NITROGEN PEROXIDE.

By L. Bell.

As a preliminary to a more important investigation, I recently had occasion to make a quantitative examination of the absorption bands of nitrogen tetroxide, and obtained results which are of some interest, both as concerning the general laws of gaseous absorption and the special properties of the gas. The definite object in view was the determination of the amount of light actually absorbed in passing through a given column of the gas in question under standard conditions. For this measurement special apparatus had to be devised, since the method used by Vierordt in his similar investigation of the absorption of liquids offers serious mechanical difficulties. Recourse was therefore taken to polarisation, and the apparatus was arranged in the following manner: An ordinary laboratory spectroscope, fitted with a prism for comparison, was used for the observations. Directly in front of the slit was a tin tank with glass ends which contained the absorption tube for the gas. This tank was filled with water so that the gas could be studied at various temperatures. Facing the comparison prism was a pair of Nicol's prisms furnished with a divided circle and a mirror, by which light from the same gas-jet that illuminated the absorption tube could be thrown through the Nicol's prisms upon the comparison prism, and thus on the upper half of the slit. The absorption tube was 10 cm. long in all the experiments. The usual eye-piece was replaced by one having an adjustable slit at its focus. The method of using the apparatus was as follows:

The Nicol's prisms were placed parallel, and the tank of water with the empty absorption tube was placed in position. The light was then arranged, by means of shifting its place and adjusting the mirror, so that it was of the same intensity throughout the field, whether coming directly through the slit or through the Nicol's prisms. The light through the tank formed the upper, and that through the Nicol's prisms the lower half of the field. Then the nitrogen peroxide was admitted to the absorption tube, and one of the absorption bands accurately covered by the slit in the eye-piece. The analyser was then rotated till the upper and lower parts of the field were again of the same intensity, and the angle read off the divided circle. The absorption coefficient was then computed directly

10cm at 750 m.m.
W l. 6000.

Variation of Absorption by Temperature

Constant Pressure.

Fig. 2.

FIG. I.
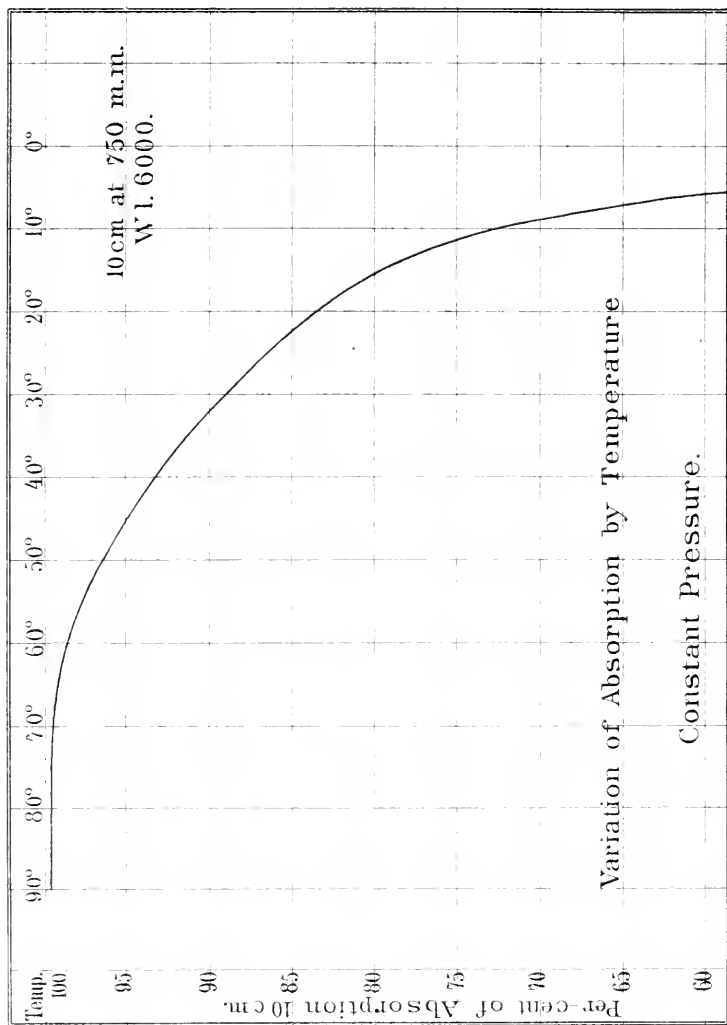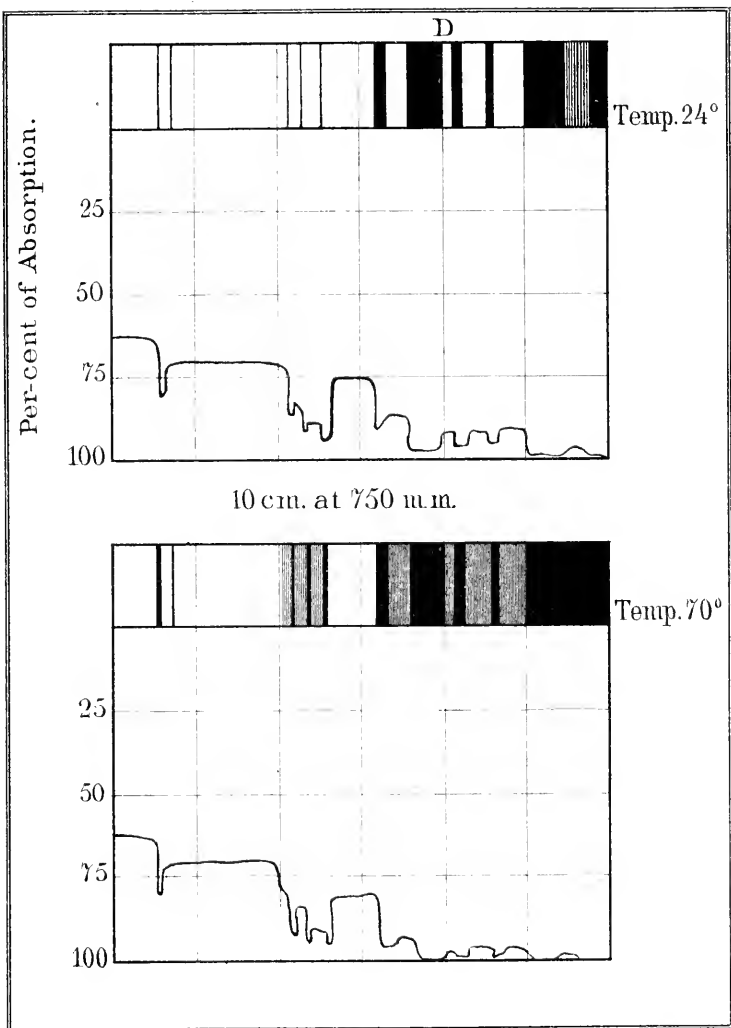
from the law of Malus, $I = \frac{\varepsilon}{2} \sin^2 a$. For since a was reckoned

from the parallel position of the Nicol's prisms, and $\frac{\varepsilon}{2}$ becomes

unity, $k = \sin^2 a$.

The general laws of absorption can be easily tested by this apparatus, but in the experiments only nitrogen peroxide was studied. The gas was made by heating lead nitrate, and was consequently diluted with oxygen, which, however, was advantageous in these preliminary investigations, as it kept the nitrogen peroxide from condensing readily and allowed the use of low temperatures. k was thus determined approximately for every five degrees from 0° to 100°. Small errors were produced by some uncompensated elliptical polarisation in the comparison prism and by possible impurities in the gas. k was obtained as above for all the bands allowing examination through such a range of temperature, and in the case of one, that at $w.$ $l.$ 6000, the readings were numerous enough to permit the construction of a tolerably accurate curve. All the observations were made at constant pressure.

Fig. 1 shows the change in the spectrum produced by change of temperature, the curve giving the amounts of light absorbed.

Fig. 2 shows the progressive changes in the band at $w.$ $l.$ 6000.

At 0° the gas was of a very pale orange color, and gradually darkened with heating till at 100° it was dark red. As is well known, this change of color is accompanied by a gradual change from the molecular form N_2O_4 to NO_2. The changes produced in the absorption spectrum by this change of composition are by no means well known. Lockyer[1] states that there is a marked change from the spectrum of the one molecular form into that of the other, while Roscoe and Schorlemmer[2] state that the change in color cannot be recognised by any equally striking change in the spectrum. It is the object of these notes to throw, if possible, a little light on this matter. Let us look at the data already known.

First. The liquefied gas forms colorless crystals at 9°, and while the liquid just above this temperature is colorless, it gradually changes color up to its boiling point.

Second. Deville and Troost[3] have shown that while the gas at 140° consists almost entirely of NO_2, it is not completely reduced to N_2O_4 at its boiling point, 22°.

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[1] Nature **10**, 89.   [2] Treatise on Chemistry **1**, 427.   Comp. Rend. **64**, 257.

Third. The vapor density of the gas, as determined by Playfair and Wanklyn,[1] shows that even at $0°$ it consists in part of NO_2.

Fourth. M. Gernez[2] has shown that the absorption spectrum of the liquid gas consists of the principal bands of the gaseous spectrum.

In my own experiments it appeared,

First. That while there is a very striking increase of both general and selective absorption produced by heating, none of the bands disappear at a high temperature. Some of the gas was even sealed up in a glass tube and heated in the flame of a Bunsen burner till the glass softened, but the bands were still permanent. As the tube was rather small in diameter, the actual appearance of the spectrum at this temperature was singularly like that of a longer column at $0°$.

Second. The determinations of k show that none of the bands increase in darkness when the temperature falls; k for each band increasing with the temperature.

Third. The rate of variation of k points to the complete disappearance of absorption at a temperature not far below $0°$.

Now what inference can we draw from these facts? Evidently this : It is highly probable that nitrogen peroxide in the molecular form N_2O_4 produces no absorption spectrum at all.

If it had a spectrum the absorption would certainly increase with the amount present, *i. e.* the length of column. But no such increase takes place, and the well-known bands remain at a temperature where it is certain that N_2O_4 is absent. Hence we may conclude that the absorption spectrum of nitrogen peroxide is entirely due to the molecular form NO_2, and that in the form N_2O_4 (as in the crystals) the compound is colorless.

In this case it is clear that the effect of the presence of N_2O_4 is simply dilution. Therefore the amount of NO_2 in the compound at any given temperature is measured by the absorption at that temperature. Hence the percentage of NO_2 can be estimated from the measured absorption at a temperature where the composition is known, as at $100°$ from Deville's experiments. Probably the best method would be graphical interpolation from measurements of the absorption of columns of $1, 2, 3 \ldots$ cm. of gas. I shall hope eventually to apply the above method in connection with an accurate determination of the various values of k.

[1] Chem. Soc. J. **15**, 156.   [2] Comp. Rend. **74**, 465.

SPECTROSCOPIC DETERMINATION OF LITHIUM.

By L. Bell.

Various attempts at quantitative spectroscopy have from time to time been made, but in general they have not met with success.

Recently, however, I have found that such a method may be applied to certain estimations with sufficient ease and accuracy to warrant calling attention to it. Lithium, notoriously difficult to determine by the usual methods, gives such a delicate spectral reaction that it proved a particularly good subject for investigation.

The method used was as follows : A standard solution was made from lithium carbonate converted to the chloride, containing .0265 milligram of Li_2O per cc. 10 cc. of this were taken, diluted till the spectral line was just on the point of vanishing, and the volume noted. Then the solution to be estimated was diluted to the same point and its volume compared with that of the standard, when a simple proportion gave the amount of Li_2O present in it.

Several variations in the method were tried, but the best results were reached when the following precautions were taken : The solutions should be tested with a *very small* loop in the platinum wire, which should not be changed, but burned clean after each trial. The Bunsen burner should not be regulated during the experiment, and the wire should always be applied to the same part of the flame. Dilution should be continued till the line is in each case barely, though constantly, visible.

A series of determinations was made to test the accuracy of the method, the amount of lithium present being in no case previously known, and the last three being solutions made up by another person.

	Determined.	Actually present.
(1)	1.5 mg.	1.4 mg.
(2)	0.7	0.7
(3)	0 9	0.7
(4)	1.1	0.9
(5)	0.9	0.8
(6)	0.6	0.5
(7)	0.7	0.7
(8)	0.29	0.32
(9)	0.42	0.40
(10)	0.68	0.55

Parallel determinations were made of the lithium in a specimen of muscovite which gradually merged into lepidolite.

	Amount analysed.	Per cent. of Li_2O.
Analysis I,	92.8 mg.	00.88
Analysis II,	90.9	00.73
Average,		00.8

Also a single estimation of the Li in the Rozena lepidolite :

Amount analysed $= 81.1$ mg.   Per cent. $Li_2O = 5.3$.   The recorded analyses vary from 1.27 to 5.88 per cent.

The advantages of this means of determination seem to be, first, it can be used with considerable accuracy in cases where the per cent. of lithium is very small, even so small as to defy even approximation by any other method ; second, it can be readily used when the amount of the substance available is too small for ordinary analysis ; third, it is simple and rapid, as it is only necessary to get the substance into solution, and for small amounts of lithium, at least as accurate as the usual process.

The method can be used for such other elements as give distinct and persistent spectral lines, particularly thallium.   Ca, Sr, Ba, K, do not give lines sufficiently persistent except in rather strong solutions, and the same is true of Rb and Cs, while Na is so ubiquitous as to give very uncertain results.

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XXII.—INFLUENCE OF BILE, BILE SALTS AND BILE ACIDS ON AMYLOLYTIC AND PROTEOLYTIC ACTION.

BY R. H. CHITTENDEN AND GEO. W. CUMMINS.

The influence of bile and bile acids on the digestive processes of the intestinal canal has long been considered an important one, still few experiments have been made to determine the exact influence of these substances by themselves on ferment action. The form in which the main constituents of the bile exist in the intestinal canal depends naturally upon the reaction of the contents

of the intestines. If these have an acid reaction, bile acids must be present ; if alkaline, salts of these acids ; and it is fair to presume that under these two conditions the presence of bile may be productive of different effects on ferment action. Recorded observations tend to show that ordinarily the contents of the intestines possess a distinct acid reaction ; thus Schmidt-Mülheim[1] has found that in dogs fed on albuminous matter the contents of the small intestines are invariably acid, although the mucous membrane sometimes possesses an alkaline reaction. It is evident that in such cases the alkali of the bile must have combined with the acid of the chyme, which would be followed by liberation of the bile acids and partial precipitation of the same in combination with the proteid matters of the chyme. Moreover, the recorded observations of Schmidt-Mülheim tend to show that this acid condition of the contents of the intestines persists throughout the entire length of the intestinal canal. Uffelmann[2] has likewise found, in corroboration of the above, that the faeces of infants naturally nourished possess a weak acid reaction, while, on the other hand, Nothnagel,[3] as a result of 800 observations, finds that human excrement, in the case of adults, varies decidedly in its reaction, being generally alkaline, more rarely acid or neutral. It is hardly proper, therefore, to conclude that it is only necessary to study the influence of the bile acids in their free condition on ferment action, since in the passage of the ferments through the intestinal canal there are times, doubtless, when the reaction of the mass is more or less alkaline, especially in the small intestines, for some distance beyond the opening of the bile and pancreatic ducts. In either case it is an interesting point to ascertain whether the bile salts have an action at all analogous in kind or extent to that of the free acids.

Many observations[4] are recorded concerning the duodenal precipitate formed in the duodenum by the action of bile on the acid-reacting chyme. The precipitate itself has generally been supposed to consist of a mixture of syntonin, peptone and bile acids, but recent experiments of Maly and Emich[5] with pure bile acids tend to show that only the non-peptonised albuminous bodies are precipitated, viz. coagulable albumin and syntonin, and

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[1] Archiv. für Physiologie. Du Bois Reymond, 1879, p. 56.
[2] Jahresbericht für Thierchemie, 1881, p. 305.
[3] Jahresbericht für Thierchemie, 1881, p. 309.
[4] See Maly in Hermann's Handbuch der Physiologie **5**, 180.
[5] Monatshefte für Chemie **4**, 89.

these only by taurocholic acid, while peptone and " propeptone " remain in solution.   This fact lends favor to the view advanced by Hammarsten, that the object of the precipitation of the albuminous matter on the walls of the intestines is to prevent its too rapid passage through the intestinal canal, thus escaping the full action of the pancreatic juice.   The addition of taurocholic acid to a solution of peptone, Maly and Emich find, is followed by the formation of a distinct opalescence or fine dust-like precipitate, slowly changing to fine droplets.   This precipitate, however, which is doubtless the same as observed by Hammarsten and Brücke on the addition of bile to portions of a digestive mixture, does not contain, according to Maly and Emich, any peptone, but consists of taurocholic acid, possibly in a modified form.

Both of these precipitations, however, would tend to mechanically throw down, to a greater or less extent, any ferment present, and thus diminish ferment action ; but, as Maly points out, the main reason for a diminished action, in the case of pepsin, is to be sought for, not in a precipitation of the ferment, but in the formation of a compound of albumin with the bile acid, not digestible by pepsin-hydrochloric acid.   But since this precipitation, as a normal reaction in the animal body, must take place in the intestinal canal, it is equally important to ascertain the extent of its digestibility in pancreatic juice, or, in other words, to ascertain the exact influence of bile and its several constituents on the proteolytic action of trypsin as well as on the action of pepsin and on amylolytic action.

The only data bearing on these points are the recent experiments of Maly and Emich, who have found that 0.2 per cent. taurocholic acid hinders the digestive action of pepsin-hydrochloric acid, while 1 per cent. glycocholic acid is without influence.   The same investigators likewise state that 0.1 per cent. taurocholic or glycocholic acid stops the amylolytic action of the pancreas ferment, and that 0.2 per cent. taurocholic acid or 1 per cent. glycocholic acid will completely stop the amylolytic action of the salivary ferment.

Our experiments on this subject were commenced before the above results were published, and we have continued them, since we wished to ascertain also the influence of the bile salts, and also the effects of both salts and acids, as well as the bile itself, on the proteolytic ferment of the pancreas.   The results of Maly and Emich, moreover, not being quantitative, do not express the relative effects of the various percentages of bile acids used, but simply the

percentage of acid necessary to stop the ferment action under the conditions described by them.

1.—*Influence on Amylolytic Action.*

As amylolytic ferment, we have employed filtered human mixed saliva, made neutral and then diluted to a known volume. In studying the influence of the various percentages of bile salts and acids on the action of the ferment we have used a digestive mixture (50 or 100 cc.) containing 1 per cent. of starch previously boiled with water, and 2 per cent. of saliva, together with the given percentages of bile salts or acids. The extent of diastatic or amylolytic action under the varying conditions was determined in each case by estimating the amount of reducing substances, maltose and dextrose, formed during 30 minutes warming at 40° C. Further diastatic action was at once stopped by boiling the digestive mixtures, after which they were diluted to a known volume, and the reducing substances determined in a given portion of the diluted fluid by Allihn's gravimetric method.[1] The reducing substances are in each instance calculated as dextrose, and the diastatic action is expressed in the percentage of starch converted into sugar.

We first tried the influence of crystallised ox bile, since bile itself contains a small amount of a diastatic ferment. A 1 per cent. solution of nicely crystallised ox bile was made, with which the following results were obtained:

Crystallised bile.	Weight Cu in one-eighth.[2]	Total amount sugar.	Starch converted.
0 per cent.	0.0643 gram.	0.2636 gram.	23.72 per cent.
0.01	0.0630	0.2584	23.25
0.02	0.0686	0.2804	25.23
0.03	0.0693	0.2836	25.52
0.05	0.0656	0.2688	24.19
0.10	0.0734	0.3000	27.00
0.20	0.0665	0.2724	24.51
0.35	0.0447	0.1860	16.74

Here it is plain that a mixture of sodium glycocholate and taurocholate, in such proportion as they are contained in crystallised ox bile, exerts no appreciable retarding influence on amylolytic

[1] Zeitschrift für analytische Chemie **22**, 448.

[2] One-eighth of the entire digestive mixture.

action until present to the extent of 0.35 per cent. On the contrary, smaller percentages unmistakably tend to increase the diastatic action of the ferment. The solution of crystallised bile had, however, a slight acid reaction, and possibly this may have had some influence in giving the latter results. The saliva and starch were both neutral.

Experiments were next tried with sodium taurocholate alone, and also with sodium glycocholate. Following are the results:

Sodium taurocholate.	Weight Cu in one-eighth.	Total amount sugar.	Starch converted.
0 per cent.	0.0787 gram.	0.3212 gram.	28.90 per cent.
0.3	0.0030	0.0146	1.51
0.5	0.0023	0.0112	1.00
Sodium glycocholate.			
0.5 per cent.	0.0783	0.3196	28.76

It is thus plainly evident that sodium taurocholate has a very decided action on the amylolytic ferment of saliva, while the same percentage of glycocholate is entirely without effect. The retarding action of the crystallised bile is thus, without a doubt, due wholly to the taurocholate. Moreover, even smaller percentages of sodium taurocholate retard amylolytic action with almost equal energy.

The following results were obtained under like conditions as the preceding, except that the 2 per cent. of saliva employed was not neutralised:

Sodium taurocholate.	Weight Cu in one-fourth.	Total amount sugar.	Starch converted.
0 per cent.	0.0590 gram.	0.1212 gram.	21.81 per cent.
0.14	0.0079	0.0192	3.45
Sodium glycocholate.			
0.20 per cent.	0.0758	0.1548	27.86

Thus even 0.14 per cent. of sodium taurocholate under these conditions almost entirely stops amylolytic action. The smaller percentage of glycocholate, however, causes the same increased amylolytic action observed with the smaller percentages of crystallised bile.

With the bile acids the following results were obtained. The glycocholic acid used was a nicely crystallised specimen prepared

from ox bile, while the taurocholic acid, prepared from the same source, was amorphous :

Per cent. bile acid.	Weight Cu in one-fourth.	Total amount sugar.	Starch converted.
0	0.0694 gram.	0.1420 gram.	25.56 per cent.
0.01 taurocholic	0.0753	0.1538	27.68
0.05	0.0783	0.1598	28.76
0.10	0.0060	0.0146	2.63
0.20	0		
0.05 glycocholic	0.0523	0.1082	19.47
0.10	0.0095	0.0234	4.21
0.20	0.0056	0.0136	2.44
0.50	trace		
1.00	0		

It is thus seen that 0.1 per cent. taurocholic acid prevents amylolytic action almost entirely, while 0.2 per cent. does not allow the conversion of any starch into sugar. This agrees exactly with the results obtained by Maly and Emich.[1] These same investigators, however, found only a trace of amylolytic action in the presence of 0.05 per cent. taurocholic acid, a result which does not agree with what we have found, working, however, under somewhat different conditions.

The presence of 1.0 per cent. glycocholic acid entirely prevents the conversion of starch into sugar, while 0.5 per cent. allows only the smallest amount of diastatic activity. Maly and Emich likewise found that 1.0 per cent. glycocholic acid stopped the diastatic action of saliva.

We have repeated the last series of experiments in part, using, however, normally alkaline saliva instead of neutralised.

Per cent. bile acid.	Weight Cu in one-fourth.	Total amount sugar.	Starch converted.
0	0.0590 gram.	0.1212 gram.	21.81 per cent.
0.1 glycocholic	0.0107	0.0258	4.64
0.2	0.0057	0.0139	2.50
0.1 taurocholic	0.0052	0.0126	2.26

These results agree exactly with the preceding, and both together plainly show that only small percentages of bile acids are required to entirely prevent the amylolytic action of saliva.

[1] *Loc. cit.* 118.

Assuming that the amylolytic ferment of the pancreatic juice is similar in its nature to the ferment of saliva, it would follow from our experiments that whether the contents of the intestines are acid or alkaline, the presence, beyond a certain percentage, of taurocholic acid, either as free acid or as a taurocholate, would tend to diminish amylolytic action. Very small percentages, however, would have little, if any, retarding effect, indeed might even increase amylolytic action. As to glycocholic acid, the free acid is much more powerful in its action on the amylolytic ferment than the sodium salt of the acid.

Considering these results in the light of a possible application to changes in the intestinal canal, it becomes an interesting point to ascertain whether bile itself exerts the same influence on amylolytic action as the bile salts. Moriggia and Battistini[1] state that while bile mixed with chyme gives a precipitate which, among other things, contains mucin, bile acids and pepsin, thus hindering gastric digestion, it does not, on being mixed with saliva, hinder its amylolytic action. This they found to be the case both with bile containing mucin and with bile from which the mucin had been removed by acidifying. We have, therefore, made the following experiments with fresh ox bile containing 7.46 per cent. of solid matter. The digestive mixtures contained as before 1 per cent. of starch, 2 per cent. of neutral saliva, and were warmed at 40° C. for 30 minutes :

Ox bile.	Weight Cu in one-eighth.	Total amount sugar.	Starch converted.
0 per cent.	0.0753 gram.	0.3072 gram.	27.64 per cent.
2.0	0.0875	0.3568	32.11
5.0	0.0690	0.2824	25.41
10.0	0.0719	0.2944	26.50
20.0	0.0770	0.3144	28.30

Here, in close accord with what has been found before, the presence of a small percentage of bile causes increased amylolytic action ; larger percentages, however, have little, if any, effect ; certainly not such an effect as would be expected from the known action of the bile salts. The bile itself possessed to a slight extent, diastatic action ; 20 cc. of the bile (20 per cent.) converting 4.53 per cent. starch into sugar in 30 minutes. This,

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[1] Jahresbericht für Thierchemie, 1876, p. 196.

however, could hardly account for the increased amylolytic action noticed above in the presence of 2 per cent. of bile. Wittich[1] and also Hofmann have noticed the occasional diastatic action of bile, Wittich even extracting the ferment from human bile by his glycerine method. Gianuzzi and Bufalini[2] have shown that the action varies considerably in bile from different animals and individuals, and without any apparent dependence upon the nature of the food. Ewald[3] states that the diastatic capacity of bile appears to be slight in all cases, and is not found in bile which has stood for some time. We have found, however, in bile from several animals considerable diastatic power; thus in one sample of fresh sheep's bile, 25 cc. (25 per cent.) converted 24.33 per cent. of starch into sugar in 30 minutes at 40° C. We have likewise found great variation in diastatic power, varying, expressed in the percentage of starch converted into sugar under the conditions described, from 4 to 24 in the case of herbivorous animals. We have also noticed in bile from sheep and oxen the presence of a small amount of sugar, or at least a substance capable of reducing Fehling's solution. In one instance the amount was not inconsiderable; 25 grams of ox bile yielding, by Allihn's method, 0.040 gram metallic copper, equal to 0.0209 gram dextrose or 0.08 per cent. Naunyn, we believe, has already claimed the presence of sugar in bile.

While we know then that the bile acids and bile salts by themselves retard very decidedly the amylolytic action of ptyalin, it would appear that the retarding influence of the latter may be, in part at least, counteracted by other substances naturally present in the bile.

2.—*Influence on the Proteolytic Action of Pepsin.*

It has long been known that bile has a retarding action on pepsin digestion, and Maly and Emich have recently shown the percentages of bile acids necessary to bring the action of pepsin to a standstill. We have, however, in addition, experimented with bile itself, and as in the case of the amylolytic ferment, have endeavored to study the influence of the bile acids quantitatively. The method employed for measuring proteolytic action is one frequently used in this laboratory, and which has invariably given satisfactory

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[1] Jahresbericht für Thierchemie, 1872, p. 243.
[2] Jahresbericht für Thierchemie, 1876, p. 197.
[3] Lectures on Digestion. Amer. ed. p. 77.

results. The only feature which calls for description is the preparation of the proteid matter to be digested. The material consists of carefully selected and thoroughly washed blood fibrin. All soluble matters are removed by successive extraction with boiling water, cold and boiling alcohol, and finally with cold and warm ether. The fibrin is thus obtained in a perfectly friable condition and can easily be ground to a coarse powder. It is then dried at 100–110° C. This material is well adapted for quantitative experiments with pepsin-hydrochloric acid ; the residue remaining after a digestion can be rapidly filtered with the aid of a pump, and can be easily freed, by washing, from peptones and other soluble products of digestion.

The gastric juice employed in the experiments consisted of a hydrochloric acid solution of a glycerine extract of pig's stomach, in the proportion of 10 grams glycerine extract to one litre of 0.2 per cent. hydrochloric acid. 50 or 100 cc. of this pepsin-hydrochloric acid were employed in each experiment, to which was added 1 or 2 grams of the dried fibrin (1 per cent.), together with the given percentage of bile or bile acids.

We first tried the influence of bile itself, using fresh ox bile, slightly alkaline in reaction and containing 10.02 per cent. of solid matter.

The digestive mixtures were warmed at 40° C. for two hours, then filtered at once and the undigested residue washed thoroughly,[1] and then dried at 100° C. until of constant weight. Following are the results of the first series of experiments, with 2 grams of fibrin and 100 cc. of gastric juice :

Bile in digestive mixture.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.1957 gram.	90.21 per cent.
0.25	0.1890	90.55
0.50	0.2050	89.75
1.00	0.2234	88.83
3.00	0.5453	72.73
5.00	0.7642	61.84

[1] In all of the pepsin-hydrochloric acid digestions the presence of bile or bile salts naturally causes more or less of a precipitate, dependent in amount upon the percentage of bile and also upon the amount of digestive products. In washing the undigested fibrin it was of course necessary to remove this precipitate. This was accomplished by pouring over the precipitate on the filter 50 cc. of 0.5 per cent. potassium hydroxide and then washing with water until the alkali was wholly removed. The following experiment shows that under these conditions the alkali affects the swollen fibrin but little, if any. Two portions of fibrin of 2 grams each were warmed with 100 cc. of 0.2 per cent. HCl for 30 minutes, then filtered and one washed with water alone, the other with water and alkali. The first gave 1.9272 grams dried residue, the other 1.9155 grams.

A second series, tried under the same conditions, but with larger percentages of bile, gave the following results:

Bile in digestive mixture.	Weight of undigested residue.	Fibrin. digested.
0 per cent.	0.1979 gram.	90.10 per cent.
0.25	0.2456	87.72
0.50	0.1927	90.36
9.00	1.1955	40.22
13.00	1.6611	16.94
16.50	1.7812	10.94
20.00	1.9241	3.29

From these two series of experiments it is evident that the presence of bile, from 1 per cent. upward, causes diminished proteolytic action, the retarding effect being proportionate to the amount of bile present. 20 per cent. of bile stops the action under these conditions almost completely. It is fair to presume, therefore, that the reflux of but a small amount of bile into the stomach would be productive of a diminished proteolytic action.

These results therefore agree with the older statements of Brücke, Hammarsten and others to the effect that bile added to a gastric digestion has the effect of bringing the proteolytic action to a standstill.

We next tried the influence of the individual bile acids with the following results:

Taurocholic acid.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.1311 gram.	86.89 per cent.
0.025	0.1461	85.39
0.050	0.2200	78.00
0.100	0.2421	75.79
0.200	0.2668	73.32
0.500	0.3579	64.21

Here it is seen that the smallest percentage of taurocholic acid added produces a distinct effect on proteolytic action, and in the next series of experiments still smaller percentages of acid caused an equally marked effect. In both series of experiments the mixtures were warmed at 40° C. for 1 hour and 30 minutes.

Taurocholic acid.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.1499 gram.	85.01 per cent.
0.010	0.1819	81.81
0.015	0.1900	81.00
0.020	0.2947	70.53
0.050	0.3110	68.90

Adding the taurocholic acid to the digestive mixture in the form of a sodium salt has the effect of diminishing still further the action of the ferment; doubtless a larger percentage of the acid remains in solution in this case.

Taurocholic acid.	Weight of undigested residue.	Fibrin digested.
0 per cent.	0.2059 gram.	79.41 per cent.
0.1	0.6198	38.02
0.2	0.6426	35.74
0.5	0.6475	35.25

Maly and Emich found that 0.2 per cent. taurocholic acid entirely stopped the action of pepsin; in our experiments, however, ferment action was still manifest even in the presence of 0.5 per cent. acid. Whether this difference in result is due to difference in the acid used, or to difference in method, we cannot say. Glycocholic acid we found to be entirely without influence on the action of pepsin, as did also Maly and Emich.

3.— *The Proteolytic Action of Trypsin in Neutral, Alkaline and Acid Solutions.*

The trypsin solution was prepared according to Kühne's method,[1] from dried pancreas freed from fat; the solution after neutralisation always contained some sodium salicylate, sufficient to prevent putrefaction during short digestive periods. According to Kühne,[2] trypsin acts quite energetically, both in neutral and salicylic acid solutions, but most energetically when the pancreatic solution contains 0.3 per cent. sodium carbonate. According to Heidenhain[3] the action of definite percentages of sodium carbonate varies with the amount of ferment.

We have tried quantitative experiments, as a preliminary to studying the influence of bile, with the following results;[4] the mixtures were warmed at 40° C. for 3 hours and 40 minutes, and contained 2 per cent. of fibrin:

[1] Untersuchungen aus der physiolog. Inst. d. Universität Heidelberg **1**, 222.

[2] *Ibid.* p. 223.   [3] Pflüger's Archiv **10**, 576

[4] The pancreatic juice was prepared from 20 grams dry pancreas, and finally diluted to 1000 cc. 50 cc. were used in each digestion with 1 gram of pure fibrin.

Reaction of the fluid.	Weight of undigested residue.	Fibrin digested.
neutral,	0.2312 gram.	76.88 per cent.
0.1 per cent. Na_2CO_3,	0.1570	84.30
0.2	0.0925	90.75
0.3	0.0772	92.28
0.4	0.0426	95.74
0.5	0.1038	89.62
0.1 per cent. salicylic acid,	0.5651	43.49

With a larger percentage of fibrin and a longer period of digestion the results are somewhat different. The following were obtained with 4 per cent. fibrin in 6 hours and 40 minutes at 40° C.:

Reaction of the fluid.	Weight of undigested residue.	Fibrin digested.
neutral,	0.3785 gram.	62.15 per cent.
0.1 per cent. Na_2CO_3,	0.2581	74.19
0.2	0.1395	86.05
0.3	0.1588	84.12
0.4	0.1629	83.71
0.5	0.1318	86.82
0.1 per cent. salicylic acid,	0.4728	52.72

An average of the two series of results plainly shows that there is but little difference in digestive action in the presence of 0.2–0.5 per cent. sodium carbonate, although in a given solution a change in the percentage of alkali is at once manifest, to a slight extent, in the amount of fibrin digested. Greatly increased percentages of alkaline carbonate materially diminish the action of the ferment, as the following series of experiments indicate ; the mixtures were warmed for 2 hours at 40° C. :

Reaction of the fluid.	Weight of undigested residue.	Fibrin digested.
neutral,	0.5863 gram.	41.37 per cent.
0.5 per cent. Na_2CO_3,	0.1584	84.16
1.0	0.3760	62.40
2.0	0.7010	29.90
3.0	0.7892	21.08
4.0	0.8373	16.27
5.0	0.8608	13.92

The difference in action between a neutral trypsin solution and a solution containing salicylic acid is quite noticeable, at the same time it is evident that in the acid-reacting fluid the trypsin simply

acts more slowly, and if time be given, the action will approach
more closely to that of the neutral solution. It is of course under-
stood that the salicylic acid in the above experiments does not exist
in the free state, but in combination with the proteid matter present,
and doubtless in most of the experiments recorded, where trypsin
has been exposed to the action of small fractions of a per cent. of
acid, no free acid has been present, but only varying percentages of
acid-proteids.[1] Kühne[2] has pointed out that hydrochloric acid
above 0.05 per cent. is injurious to the action of trypsin, and
Heidenhain[3] has shown that the addition of 0.1 per cent. hydro-
chloric acid to an aqueous extract of the pancreas stops its action.
C. A. Ewald,[4] however, found that while pepsin-hydrochloric acid
destroyed trypsin, trypsin could digest fibrin in the presence of 0.3
per cent. hydrochloric acid. Mays[5] likewise found that trypsin
digestion could take place in the presence of 0.3 per cent. hydro-
chloric acid, but only when a relatively large proportion of fibrin
was present, and in corroboration of Kühne's statement, he showed
that trypsin could be destroyed both by pepsin and dilute hydro-
chloric acid. Engesser[6] found that a pancreatic juice did not lose
its tryptic power by two hours warming with a gastric juice con-
taining 0.5 per cent. hydrochloric acid. Langley,[7] on the contrary,
has shown that a glycerine extract of the pancreas loses a very
appreciable amount of trypsin when warmed for two and a half
hours with 0.05 per cent. hydrochloric acid. Lindberger,[8] working
with an alcohol precipitate from a glycerine extract of ox pancreas,
in which there would naturally be present but a small amount of
proteid matter in addition to the trypsin, found that in the presence
of 0.1 per cent. hydrochloric acid the ferment was entirely
without action, and even in the presence of 0.012 per cent.
hydrochloric acid, fibrin was much more slowly dissolved than by
a neutral trypsin solution. Lindberger, moreover, found that
weaker acids, as acetic and lactic, had a much different effect than
the stronger hydrochloric acid; thus with dilute acetic acid
digestion of the fibrin was almost as rapid as with a neutral solution
of trypsin, while with small amounts of lactic acid, the ferment

[1] See Danilewsky. Centralbl. med. Wiss. 1880.

[2] Vehr. Naturhist. med. Vereins zu Heidelberg, 1877, p. 193.

[3] Pflüger's Archiv **10**, 578.   [4] Jahresbericht für Thierchemie, 1880, p. 297.

[5] Untersuch. a. d. physiolog. Inst. d. Univ. Heidelberg **3**, 378, 1880.

[6] Jahresbericht für Thierchemie, 1880, p. 297.   [7] Journal of Physiology, Vol. 3, No. 3.

[8] Jahresbericht für Thierchemie, 1883, p. 281.

action was even more energetic than in a neutral solution. There is, however, no guarantee that in these experiments free acid was present.[1]

We have found that *free* acids, even when present in small percentages, completely stop the proteolytic action of trypsin; and that when considerable albuminous matter is present, the action of trypsin is much hindered by the addition of acid to a neutral solution even before the proteid matters present are saturated with acid. 0.1 per cent. *free* salicylic acid, in the presence of proteids already saturated with the acid, allows no proteolytic action whatever. On the other hand, a sufficient amount of proteid matter just saturated with hydrochloric acid, no free acid being present, will almost completely stop the action of trypsin. Proteid matter, however, only partially saturated with acid has a much smaller retarding action. This, doubtless, was the condition of the mixtures in Mays' and Engesser's experiments above referred to, for, as Mays states, the ferment could act in the presence of 0.3 per cent. hydrochloric acid only when a relatively large proportion of fibrin was present.

A pancreatic juice prepared from 20 grams of dried pancreas by warming it at 40° C. with 200 cc. 0.1 per cent. salicylic acid, etc., was finally made exactly neutral and diluted to 500 cc.; 25 cc. of this solution required 7.5 cc. of a 2.0 per cent. solution of salicylic acid to completely saturate the proteids present,[2] the excess of free acid necessary to give the tropaeolin reaction being deducted.

Three digestive mixtures were made as follows :

1. 25 cc. of the neutral pancreatic solution $+$ 50 cc. water.

2. 25 cc. of the same pancreatic solution $+$ 7.5 cc. 2.0 per cent. salicylic acid solution $+$ 17.5 cc. water. The mixture was acid to test papers, but gave no reaction with tropaeolin. It therefore contained no free acid, but 0.3 per cent. of combined acid.

3. The same as No. 2, but 2.5 cc. more of 2.0 per cent. salicylic acid, so that the solution contained, in addition to the acid proteids, 0.1 per cent. free salicylic acid.

1 gram of fibrin was added to each of these and the mixtures

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[1] We have seen only the abstract of Lindberger's paper, so cannot speak positively on this point.

[2] Tested by tropaeolin oo according to the method of Danilewsky (Centralbl. med. Wiss. 1880). One drop of a solution containing 0.028 per cent. free salicylic acid gives a reddish violet color, which is, however, not permanent as in the case of hydrochloric acid, but transient. With hydrochloric acid, one drop of a 0.003 per cent. solution will give the reaction.

warmed at 40° C. for 8 hours and 40 minutes. No. 1 digested 88.34 per cent. of the fibrin; No. 2, 13.44 per cent., while No. 3 had no action whatever.

Much smaller percentages of combined salicylic acid cause an equally diminished proteolytic action; thus, in the case of a carefully dialysed juice where the proteid matter was much diminished, the digestive mixture, with its proteids wholly saturated, contained but 0.060 per cent. of combined salicylic acid; yet this mixture, in 15 hours at 40° C., digested but 17.10 per cent. of fibrin, while the same amount of the neutral trypsin solution digested 57.80 per cent. Combined hydrochloric acid has a greater hindering action than salicylic acid, as the following results show:

Pancreatic solution of trypsin.			Fibrin digested in 18 hours.
neutral,			57.80 per cent.
0.034 per cent. combined HCl + no free HCl			3.90
0.034 " "	HCl + 0.005 per ct. HCl		2.31
0.034 " "	HCl + 0.010		0.87

It is thus evident that in an ordinary digestive mixture, or even where albuminous matter is present only in limited quantity, the addition of hydrochloric or salicylic acid to a neutral solution of trypsin reduces its proteolytic action to a minimum before any free acid is present.

4.—*Influence of Bile, Bile Salts and Bile Acids on the Proteolytic Action of Trypsin.*

The addition of bile to a *neutral* pancreatic juice causes but little change in its proteolytic action, as is seen from the following results obtained with ox bile containing 8.3 per cent. solid matter:

Bile.	Wt. of undigested fibrin.	Fibrin digested.
0 per cent.	0.4118 gram.	59.82 per cent.
1.0	0.3907	60.93
10.0	0.3938	60.62

A slightly increased action is the only effect produced on the trypsin.[1] The addition of bile to an *alkaline* pancreatic juice does not produce any very different results. The following were obtained with a pancreatic juice containing 0.3 per cent. sodium carbonate and fresh ox bile containing 10.02 per cent. solid matter:

[1] Compare Heidenhain, Pflüger's Archiv **10**, 579.

Bile.	Wt. of undigested residue.	Fibrin digested.
o per cent.	0.3056 gram.	69.44 per cent.
0.25	0.3074	69.26
0.50	0.3488	65.12
1.00	0.3633	63.67
5.00	0.3278	67.22
10.00	0.3603	63.97

Here there is no increased proteolytic action, neither is there any very great retarding effect produced. Pure sodium glycocholate and taurocholate produce results similar to bile, as the following table shows. The pancreatic juice contained 0.3 per cent. sodium carbonate :

Sodium taurocholate.	Weight of undigested residue.	Fibrin digested.
o per cent.	0.2308 gram.	76.92 per cent.
0.05	0.2566	74.34
0.10	0.3048	69.52
1.00	0.2832	71.68
Sodium glycocholate.		
0.10 per cent.	0.2576	74.24
0.20	0.3154	68.46

The presence of 3.0 per cent. crystallised ox bile caused a somewhat different result, increasing the proteolytic action slightly ; thus, while the control, containing 0.3 per cent. sodium carbonate, digested 88.69 per cent. fibrin, the same trypsin solution plus 3 per cent. of crystallised bile digested in the same time 89.73 per cent. fibrin.

While bile or bile salts have but little influence on the proteolytic action of trypsin, the bile acids, even small percentages, have a much more marked effect. The following results, obtained by the addition of the bile acids to a neutral pancreatic juice, show the extent of the action :

Bile acids.	Weight of undigested residue.	Fibrin digested.
o	0.2516 gram.	74.84 per cent.
Glycocholic, 0.03 per cent.	0.1993	80.07
Taurocholic, 0.10	0.3455	65.45
0.20	0.4332	56.68
0.50	0.4170	58.30

Here, the retarding influence of taurocholic acid is very manifest, while, on the other hand, the small percentage of glycocholic acid appears to increase the action of the ferment.

In view of the possible acid-reacting character of the contents of the small intestines, it becomes an interesting point to ascertain the influence of bile on the action of trypsin in the presence of more or less combined acid. With a pancreatic juice in which the proteids were partially saturated with salicylic acid, 0.1 per cent. combined acid being present, the following results were obtained:

Bile.	Weight of undigested fibrin.	Fibrin digested.
0 per cent.	0.4822 gram.	51.78 per cent.
1.0	0.4858	51.42
10.0	0.4091	59.09

This increased action in the presence of 10 per cent. of bile accords with Lindberger's results, this experimenter having found that bile in the presence of small percentages of (combined?) acetic and lactic acids tends to diminish the retarding effect produced by the acids alone.

In the presence of combined hydrochloric acid, the bile salts produced no effects whatever; the trypsin was entirely without action.

A METHOD OF DETERMINING THE VALUE OF ZINC DUST.

By H. N. Morse.

The apparatus and method here described were devised for the purpose of determining with a reasonable degree of accuracy the volume of hydrogen which metals will yield when they are treated with acids or alkalis. The present article is, however, limited to their application to the determination of the value of zinc dust.

It is believed that the results obtained by this method will be found to compare favorably with those reached by the excellent method of Fresenius,[1] that the skill demanded of the operator is not greater, and that the time required for a determination is considerably shorter.

The apparatus (Fig. 1) consists of the following parts:

[1] Zeit. ann. Chem. **17**, 465.
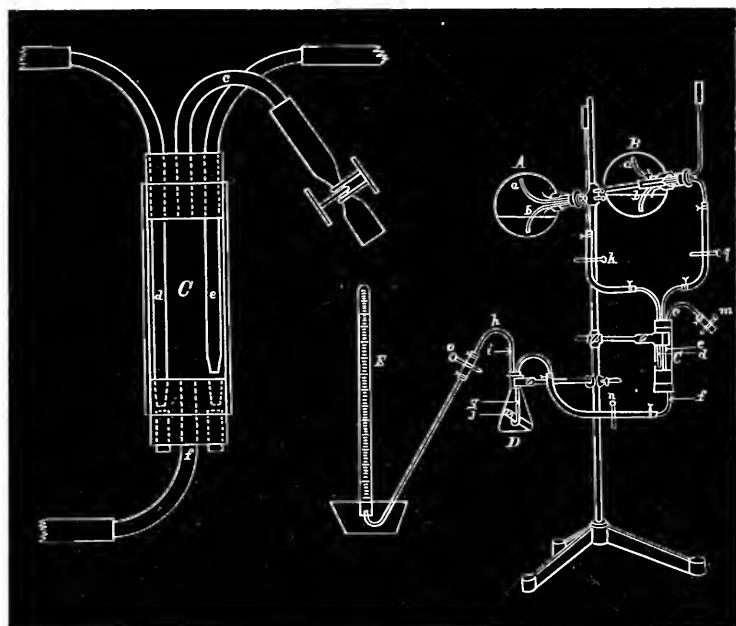
Fig. 1.

1st. Two flasks, *A* and *B*, each having a capacity of 750 or 1000 cc. One serves as a reservoir for distilled water, the other for dilute hydrochloric acid. Each flask is supplied with a rubber stopper, through which two small glass tubes *aa* and *bb* pass. The tubes *aa* connect the space above the liquids in the flasks with the outer air, and allow the gases expelled from the liquids by boiling to escape. The tubes *bb* dip under the surface of the liquids and serve to conduct them to other parts of the apparatus. The flasks *A* and *B* are filled to the level of the lower side of their necks by pulling the stoppers far enough forward to admit of the insertion of a funnel tube, the stem of which has been bent to a right angle. The contents of the flasks are boiled to expel the air absorbed in them.

2d. The arrangement *C*, which is a simple substitute for a three-way stopcock. The outer tube of *C* has an internal diameter of about 15 mm. and a length of about 70 mm.

It is supplied with two rubber stoppers, each of which has three perforations. The upper stopper carries the tube *c*, which

terminates at its lower surface; and the movable tubes d and e, which, when they are pressed down, enter corresponding holes in the lower stopper, and thus cut off the flow of liquids from A and B into C. The holes in the upper stopper through which d and e pass are lubricated with vaseline. The lower half of the holes into which d and e enter when they are pushed down is closed with glass plugs. The tubes C and d and C and e are connected by means of pieces of rubber tubing, each of which is supplied with a Mohr's pinch-cock. A short piece of rubber tubing with a pinch-cock is also slipped over the end of the tube c so that it may be opened or closed at will. The tube f terminates at the upper surface of the lower stopper, and serves to connect C with the flask in which the decomposition is effected.

To fill C from the flask A or B, the tube d or e, as the case may require, is raised, the pinch-cocks m and k, or q, are removed, and the liquid started down the tube c by sucking with the mouth at the end of the tube c. C then fills, the air being expelled through c. By closing m and opening n the liquid is made to pass on into the generating flask.

3d. An Erlenmeyer flask D, having a capacity of 50, 60 or 70 cc. The rubber stopper of this flask carries an inlet tube g and a delivery tube h, the forms and positions of which are sufficiently clear from the figure. A part of the vertical portion of the tube h should be filled with small fragments of broken glass, which may be kept in their proper position by allowing the end opening into the flask to soften and contract in the flame.

The zinc dust is placed in the small preparation tube J, and prevented from leaving the same by means of a filter of glass wool.

The tube and flask must be of such relative proportions that the open end of the former is somewhat elevated when the tube is in position in the flask. However, the space between the edge of the tube and the side of the flask must not be so great at any point as to allow the glass wool to escape from the tube. A little attention to this point is quite essential to the success of the method. The glass wool employed should be of the best quality, that is, the fibres should be long and elastic.

4th. A calibrated 100 cc. gas measuring tube E, which is filled with recently boiled, and still hot, water.

The rubber tubing employed in making the various connections should have thick walls and be of the best quality.

Tubing and stoppers which yield gas when treated with acids must, of course, be carefully avoided.[1] All rubber parts of the apparatus should be boiled in hydrochloric acid before they are used.

The determination is made in the following manner:

A weighed quantity of the zinc dust (0.200 to 0.240 gram) is placed in the bottom of the tube *J*. Enough water, which has been freed from air by boiling, to fill the tube about one-fourth full is introduced. The dust and water are then thoroughly mixed by means of a stout platinum wire or a small platinum spatula. The dust quickly subsides after the stirring has ceased, and any particles adhering to the platinum can be readily washed off by dipping it into the clear supernatant liquid.

A small bunch of glass wool, which has been freed from air by pressing it between the fingers under water, is now introduced and pressed down lightly upon the zinc dust. If it is believed that the quantity of glass wool already introduced is not sufficient to constitute a perfect filter, more is added; but an unnecessarily large quantity of the wool should be avoided, because of the obstruction which it offers to the passage of the gas out of the tube and the acid into it.

If gas bubbles lodge in or under the glass wool while it is being pressed down, they are dislodged, and brought to the surface by means of a platinum wire.

The tube having been placed in position, the whole apparatus is filled with water, and then with acid from *A* and *B*; both water and acid having been thoroughly boiled.

The acid is allowed to act for some time upon the zinc dust before heat is applied, in order that the finer material, which is most likely to be carried through the filter, may be slowly and quietly dissolved. Afterwards a small flame is placed under the flask. It generally happens that the hydrogen generated in the bottom of the tube crowds the wool up into the other end and against the side of the flask; but, if the tube and flask have been properly selected and the tube properly filled, there is no danger that either the wool or the dust will escape. The crowding of the wool into the open end of the tube, however, obstructs the entrance of the acid; but this difficulty can be remedied by occasionally applying the flame to the side of the flask directly in front of the mouth of

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[1] Much of the American rubber now offered for sale yields large quantities of gas when treated with dilute acids.

the tube. Toward the end of the operation, when the hydrogen generated is mixed with a large proportion of steam and acid vapor, the tube can be readily filled with acid by opening the pinch-cock *n*, and allowing some of the cooler acid in *C* to flow into *D*.

The alloy of lead and zinc, which appears to be a constant constituent of zinc dust, decomposes quite slowly in dilute acids, and great care must be taken not to discontinue the operation until all evolution of hydrogen has ceased.

Hydrochloric acid is preferred for this decomposition, because it decomposes the lead-zinc alloy more rapidly than sulphuric ; and because, being volatile, it dissolves the zinc dust which is lodged in the glass wool, even when the wool is not immersed in the liquid acid.

Before reading the volume of the gas collected, the tube *E* must, of course, be placed in a cylinder of water to which a little caustic soda has been added, in order to remove any carbon dioxide and vapor of hydrochloric acid which may be present.
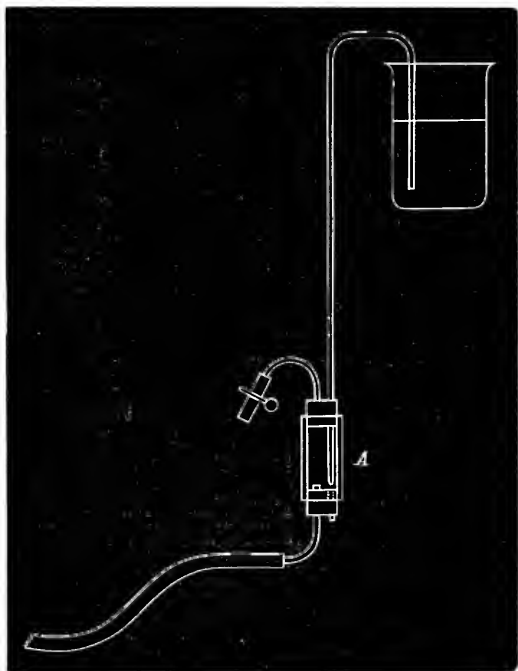
Fig. 2.

Fig. 2 represents a very simple substitute for the parts A, B and C of Fig. 1, which would probably be preferred by one who had only a small number of determinations to make. When this is used the water and acid are boiled in beakers, which are brought, one after the other, into the indicated position. The filling of A, Fig. 2, is accomplished in the same manner as that of C, Fig. 1.

The apparatus and method just described were placed in the hands of Messrs. W. H. Emerson and C. W. Hayes, students in this laboratory, to be tested with reference to the agreement of results which may reasonably be expected from them. Both used the same specimen of zinc dust. Mr. Emerson made four determinations, Mr. Hayes six. All of the results obtained by these gentlemen are recorded in the following statement:

Wt. of dust.	Vol. H_2 obtained.	Calc. wt. of Zn.	Per cent. Zn found.
0.2519 gram	77.14 cc.	0.22486 gram	88.87
0.2507	76.44	0.22282	88.80
0.20035	61.30	0.17869	89.13
0.2270	69.26	0.20188	88.93
0.2443	74.25	0.2164	88.60
0.2137	65.33	0.1904	89.10
0.2453	74.58	0.2174	88.62
0.2448	74.73	0.2178	88.97
0.2410	73.58	0.2145	88.95
0.2422	73.91	0.2154	88.94

An attempt was made to determine the value of zinc dust by amalgamating the metallic portions with mercury and weighing the amalgam. It was found that the metallic zinc contained in the dust is rapidly dissolved by the mercury in the presence of a one per cent. solution of tartaric acid, and that the quantity of hydrogen gas given off during the time required for the amalgamation is quite insignificant. Nevertheless the results were not satisfactory because of the difficulty with which the particles of dirt which collect upon the surface of the amalgam are removed.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

TWO FORMS OF APPARATUS WHICH FACILITATE THE CORRECT READING OF GAS-VOLUMES OVER WATER.

By H. N. Morse.

Every one who has had occasion to measure gases in the ordinary manner over water— that is, by raising the eudiometer above the water in the immersing cylinder until the liquid inside and outside of it stands on the same level—is familiar with a very disquieting experience. The volume of the gas quickly contracts in consequence of the cooling effect produced by the evaporation from the wet surface of the tube, which is now exposed to the air. As soon as the tube is raised into position the contraction begins; and if the condition of the atmosphere is such as to favor evaporation, it progresses very rapidly. However quickly the volume of the gas may have been noted, one rarely feels quite satisfied that the reading has not been affected by a change in temperature from this cause.
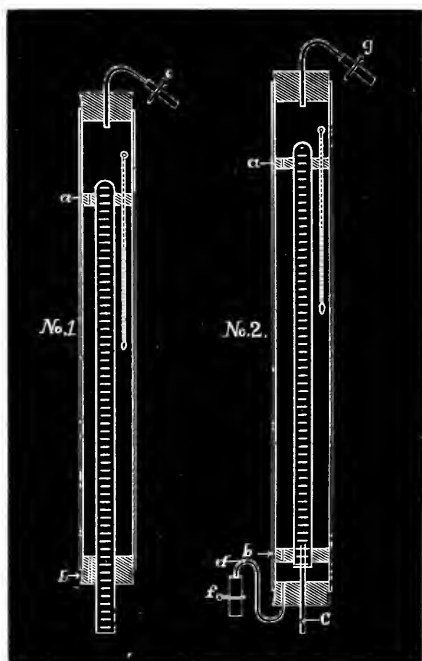
Fig. 1.   Fig. 2.

Either of the simple arrangements represented in figures 1 and 2 will obviate the difficulty. The first (Fig. 1) is to be used 'in connection with an immersing cylinder. The second (Fig. 2), without it. In both cases the eudiometer is fastened quite firmly into a clear glass tube by means of the corks *a* and *b*, all of which are perforated in order to allow the water to pass freely up and down. The corks *aa* carry thermometers. The eudiometer in No. 1 projects below, while that in No. 2 is wholly included in the jacket tube. Each apparatus is closed at the top by a stopper, through which a small glass tube passes. The lower end of No. 2 is closed by a cork, which carries two tubes *c* and *d*. The tube *c* receives the gas from the delivery tube, and conducts it into the eudiometer; while *d* serves as an overflow tube for air or water. The cork used in constructing these pieces of apparatus should be thoroughly soaked in molten paraffine.

The method of using No. 1 is as follows: it is inverted, and the eudiometer filled in the usual manner. When it is transferred to the immersing cylinder, the pinch-cock *e* is removed and the jacket allowed to fill with water. When it is desired to read the volume of the gas, the pinch-cock is replaced and the apparatus drawn up until the water inside of the eudiometer and outside of the jacket stands on the same level. The jacket remains filled with water having the same temperature as that in the cylinder, and protects the gas from any sudden changes in temperature. No. 2 is inverted, the pinch-cock *f* removed, and the whole apparatus filled with water until the tube *d* overflows; when *f* is replaced, and the remainder of the tube *c* which lies above the level of the outlet of *d* is filled.

The apparatus is now placed over the delivery tube in the usual manner. The gas having been collected, *c* is closed by means of a tightly fitting stopper, and the apparatus removed to a clamp stand and fastened in a vertical position and at a convenient height. When the volume of the gas is to be ascertained, the pinch-cock *g* is removed, and the water in the jacket allowed to descend through *d* to the proper level by opening *f*. The space in the jacket thus vacated by the water being saturated with aqueous vapor, retains for a considerable time the temperature of the water. If it is desired to treat the gas with absorbents, they can be introduced by removing the upper stopper and pouring them into

the jacket, the level of the liquid previously contained in it having been lowered to any extent which may seem expedient. The succession of meniscuses which is obtained when the liquid in the jacket is lowered to the level of that in the eudiometer, considerably facilitates the correct reading of the volume of the gas.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

AN APPARATUS FOR THE PURIFICATION OF MERCURY BY DISTILLATION IN A VACUUM.

BY H. N. MORSE.

The essential parts of the apparatus are an ordinary combustion tube, *a*, about 450 mm. long, which has been drawn out at the ends, *b* and *c*, in the manner indicated in the figure; and two pieces of barometer tubing, *d* and *e*.

b and *d* are connected by means of rubber tubing; *c* and *e* by means of a tightly fitting rubber stopper. A mercury cup is placed over each of these joints to prevent leakage.

The tube *e* projects into the large end of *c* to some distance above the stopper, in order that the lower portion of *c* may fill with mercury, and thus protect the stopper from the hot metal which falls from above.

The distance between *b* and *h* is about 770 mm. The length of the tube *e* above *i* should not be less than 825 mm.

The turned-up ends of *d* and *e* should have a length of 60 mm., or a length more than sufficient to compensate the greatest variations of atmospheric pressure.

b and *c* make such angles with *a* that they remain vertical when the front end of *a* is raised about 15 mm. (a distance equal to the internal diameter of the tube) above the back end. The apparatus is held in position by means of a wooden stand which consists of a base and two uprights, *f*, *g* and *l*; a double bracket, *m*; a brace, *n*; and a movable shelf, *j*.

The tube *a* is placed in a sheet-iron trough which rests in a groove in the upper ends of the uprights *g* and *l*. The tubes *d*

and *e* are fastened to the uprights by means of hooks and rubber stoppers or corks. The hooks should be somewhat open, so that, after slipping the stoppers out of them, the apparatus as a whole may be removed from the stand. Good hooks for this purpose are obtained by filing off the turned-in end of ordinary screw eyes.
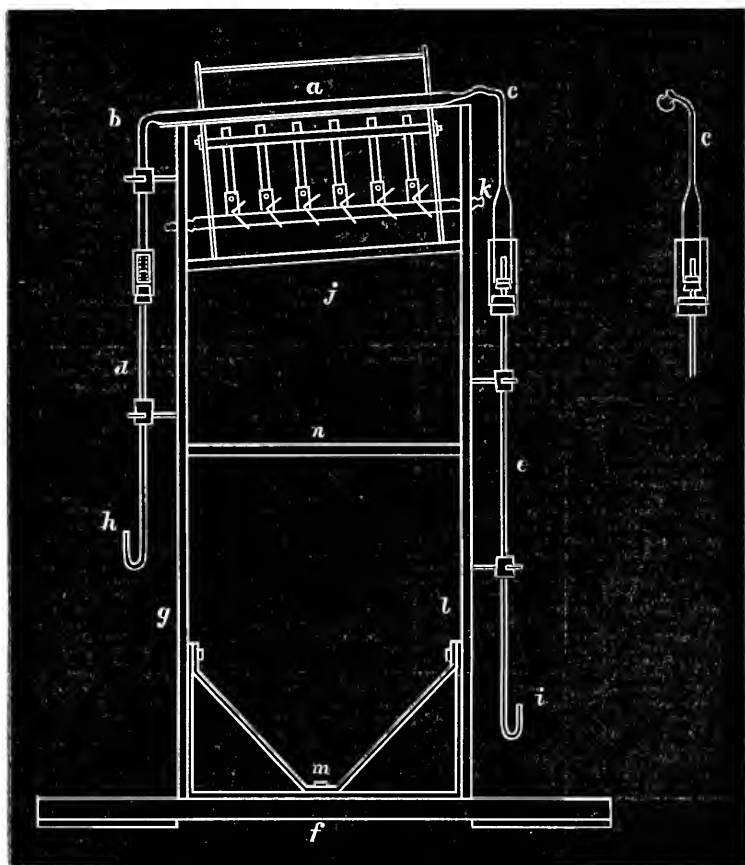
The tube *c* is turned to one side, if necessary, in order to avoid the rubber tubing through which the gas is brought into the furnace at *k*.

To set the apparatus in operation, the lower end of the tube *d* is immersed in a narrow cylinder containing some of the mercury

to be distilled. A Sprengel pump is then attached to i and the apparatus exhausted. By raising or lowering the cylinder in which h is immersed, the mercury is brought to the proper level in a; after which the lamps beneath are lighted. The flames should be made as small as possible at the beginning of the distillation, and the temperature should never be allowed to rise so high as to produce any visible commotion in the distilling mercury.

The tube c being cool during the first part of the distillation, the rubber stopper connecting c and e is not injured by the mercury which falls upon it. After the lower end of c has been once filled and the mercury has begun to descend through e, there is no danger of overheating the stopper, however rapidly the distillation may proceed.

When enough mercury has been distilled to fill e to the barometric height, the Sprengel pump is detached. The working of the apparatus is afterwards automatic. Whenever it is desired to distill a quantity of mercury, it is also necessary to place a cylinder containing it over h and light the gas under a.

The action of e and its connections being that of a Sprengel pump, the vacuum is never more than temporarily impaired.

The apparatus can also be brought into working order without the use of a Sprengel pump by attaching a long glass tube in a vertical position to h, and filling a through it to the proper level, and then distilling until a vacuum is produced.

The distillation of mercury by this arrangement is quite rapid; and when it is once in operation it requires no attention, except that of keeping the mercury in the feeding cylinder at something near the proper level. An automatic arrangement for this purpose is quite desirable.

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SOME EXPERIMENTS ON THE RELATION OF ANTI-SEPTIC POWER TO CHEMICAL CONSTITUTION.

By J. R. Duggan.

The following paper is, as the title states, simply an account of some experiments, with no attempt at anything farther; and they are offered more as a suggestion towards future work than for any value of their own. I hope that in the future they may be extended

to such a number of compounds, and with such accuracy, as to be of some use in the study of the physiological action of organic bodies whose chemical structure has been previously determined. Of course the step from the minute organisms to the vertebrate body is an immense one, but in each case we must study the action on single cells, and where these are separate and undifferentiated the conditions are much easier to control and the problem much simpler. One can scarcely hope for a perfect science by which the physiological action of a compound can always be foretold from its chemical constitution, but there is certainly reason to expect that we may in time be able to trace certain general laws that apply to classes of compounds and groups of atoms ; and with this ultimate view the following experiments have been undertaken.

The method used to determine antiseptic power consisted in adding to 10 cc. of a standard solution of beef peptones the requisite quantity of a solution of the compound and water enough to make the whole measure 20 cc. This was placed in a small flask stoppered with cotton, and heated just to boiling in order to kill any organisms present. In the case of alcohols and other easily volatile bodies, the flask was tightly corked before heating to avoid loss by evaporation. After cooling, the cotton plug was lifted with a pair of sterilised forceps, and a few drops of a culture fluid containing only *Bacillus subtilis* added to the solution. This precaution was found necessary, not so much to prevent the presence of other bacteria, as to keep out spores of penicillium and mucor. These develop readily under conditions that prevent entirely the growth of bacteria, and thus interfere with results.

A series of flasks thus prepared were placed in a warm chamber kept at about 36° C., and examined twice daily. The cloudiness of the solution was found to be the best indication of the development of the bacteria, although microscopic examinations were frequently made. The point in view has been to find what quantities of the various substances under consideration would give an equal restraining influence, and not to determine the amount that entirely prevents development. The approximate standard was a flask giving slight cloudiness in 48 hours and considerable in 72.

The method in itself seems very simple, but in practical working several difficulties introduce themselves, and interfere considerably with the accuracy and reliability of results. For example, some of the flasks, especially those containing phenol and the acids of

the marsh gas series, frequently show a slight cloudiness which does not increase, or at least very slowly, on standing. It has occurred to me that this might be due to the products of putrefaction formed, and which thus increase the amount of these agents to an extent that prevents further development.

The following table is a list of the substances whose restraining influence has been determined with approximate accuracy, and of the amounts required in parts per 10,000 of the solution:

Oxybenzoic acids, $C_6H_4(COOH)(OH)$.

Salicylic acid	$(1:2)$	.	.	4
Oxybenzoic acid	$(1:3)$	.	.	6
Paraoxybenzoic acid	$(1:4)$	.	.	8

Phenols, $C_6H_5(OH)_x$.

Phenol, $C_6H_5(OH)$	.	.	20
Pyrocatechin, $C_6H_4(OH)_2$ $(1:2)$		.	20
Resorcin, $C_6H_4(OH)_2$ $(1:3)$	.	.	25
Hydroquinone, $C_6H_4(OH)_2$ $(1:4)$	.		30
Pyrogallol, $C_6H_3(OH)_3$	.	.	.	15

Alcohols, $RCH_2(OH)$.

Methyl alcohol, $CH_3(OH)$	.	.	300
Ethyl alcohol, $C_2H_5(OH)$	.	.	500
Propyl alcohol, $C_3H_7(OH)$ normal	.		200

In addition to the above the three acids, formic, acetic, and propionic, have been experimented upon to determine both their antiseptic and their germicide power. Accurate conclusions have not yet been reached on their restraining influence, but it is evidently considerable, and is not in the order of their corresponding alcohols, propionic being lowest in the series, and formic the highest. Their germicide power was tested by exposing spores of *B. subtilis* to their action for two hours. The amounts required to destroy these were of formic, 7 per cent.; of acetic, 9 per cent.; and of propionic, 12 per cent. It will be seen that these figures are pretty nearly in an inverse ratio to the acidity of these acids, that is, the amount of any base which they can saturate.

The first two classes in the above table seem to show that ortho compounds are the most antiseptic, and the para the least so,

but it will be necessary to examine a larger number of substances before this conclusion can be stated as a general one.

It will be noticed that the alcohols show a peculiar order, for which I can suggest no explanation. A few other surmises, such as the influence of the hydroxyl group, might be offered, but I prefer to leave these for another paper, in which it is intended to include experiments in a much larger number of compounds on which to base conclusions.

JOHNS HOPKINS UNIVERSITY.

ON SOME PROPERTIES OF PHENYLSULPHONACETIC ETHERS.[1]

BY ARTHUR MICHAEL AND GEORGE M. PALMER.

II.

In the first communication on this subject it was shown that in ethyl phenylsulphonacetate the combined negative influence of phenylsulphuryl and ethylcarboxyl on methylene sufficed to render one of the hydrogens of the latter group replaceable by sodium ; and, by the action of benzylchloride on the sodium derivative, benzyl could be introduced in place of sodium. In the present note we shall show that a method of obtaining substitution derivatives of cinnamic acid may be based on the properties of above compounds, and that alkyl iodides act on the sodium derivatives in the same manner as benzylchloride, forming alkylphenylsulphonacetates. The examination of this class of compounds has called renewed attention to their similarity with acetylalkylacetates, inasmuch as when they are heated with alkalis they decompose into phenylalkylsulphones and alkaline carbonates : a reaction corresponding to the decomposition of acetylalkylacetic ethers into alkylacetones and carbonates.

Action of alcoholic caustic potash on phenylsulphonacetic ether.

Two grams of the ether and four grams of caustic potash were dissolved in about ten grams of alcohol and the solution heated

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to 140° for five hours. The contents of the tube was evaporated on a water-bath, and water added to the residue. An insoluble oil remained, which soon solidified, and was purified by crystallisation from hot water. The analysis gave the following results:

0.3878 gram of substance gave 0.7612 gram of CO_2 and 0.1858 gram of H_2O.

	Theory for $C_6H_5SO_2CH_3$.	Found.
C	53.8	53.5
H	5.1	5.3

The substance crystallises from hot water as tabular plates, and melts at 88°. It is identical with the phenylmethylsulphone obtained synthetically from sodium phenylsulphinate and methyl iodide,[1] and its formation may be represented as follows:

$$C_6H_5SO_2CH_2COOC_2H_5 + 2KOH$$
$$= C_6H_5SO_2CH_3 + K_2CO_3 + C_2H_6O.$$

This sulphone has been obtained by four different methods:[1] by the action of sodium phenylsulphinate on methylene-iodophenylsulphone; by the action of alkylsodiumoxides on the same compound; by the action of methyliodide on sodium phenylsulphinate; and by the action of alkalis on phenylsulphonacetic ether. It is evident that the introduction of phenylsulphuryl in the methyl of acetic acid shows itself in loosening the affinity between the two linked carbon atoms; an effect which is also produced by other negative groups, as acetyl and ethylcarboxyl.

Action of ethyl iodide on sodium phenylsulphonacetic ether.

To a solution of one gram of sodium in absolute alcohol, an alcoholic solution of 10 grams of phenylsulphonacetic ether (1 mol.) was added, and, finally, 6.8 grams of ethyl iodide. The mixture was heated in a flask connected with reflux-cooler until it had lost its alkaline reaction; it requiring from five to six hours for the quantities taken. The alcohol was then distilled off, the residue poured into cold water, and allowed to stand until it became solid. The substance was purified by repeated crystallisation from dilute alcohol. The sulphur estimation gave the following result:

0.3332 gram of substance gave 0.3096 gram of $BaSO_4$.

	Theory for $CH \overset{C_2H_5}{\underset{COOC_2H_5}{-SO_2C_6H_5}}$	Found.
S	12.5	12.7

[1] This Journal **6**, 253.

Ethylphenylsulphonacetic ether crystallises from dilute alcohol as rhombic prisms, melting at 62°. It is readily soluble in ether, benzene, ethylacetate, moderately in ligroin, insoluble in water. The addition of sodium ethyl oxide to the alcoholic solution forms a precipitate of the sodium derivative which is more soluble than that of phenylsulphonacetic ether. This compound heated with alcoholic potash undergoes a decomposition similar to that of phenylsulphonacetic ether. Five grams of the ether and seven grams of caustic potash were dissolved in alcohol and heated in a sealed tube for five hours at 140°. The product was treated as already described for methylphenylsulphone, with the difference that the residue was purified by crystallisation from ligroin to which a few drops of acetic acid were added.

0.3247 gram of substance gave 0.6922 gram of CO_2 and 0.1877 gram of H_2O.

0.3693 gram of substance gave 0.7940 gram of CO_2 and 0.2237 gram of H_2O.

	Theory for $C_6H_5SO_2C_3H_7$.	Found.	
C	58.7	58.1	58.7
H	6.5	6.4	6.7

Propylphenylsulphone crystallises from ligroin as large rhombic plates, melting at 45°, and has an odor resembling that of crotonic acid. It is insoluble in water, but readily soluble in ether, chloroform, alcohol and acetic acid.

The formation of the sulphone may be represented as follows:

$$\begin{matrix} C_6H_5SO_2 \\ C_2H_5 \end{matrix} > CH - COOC_2H_5 + 2KOH$$
$$= C_6H_5 - SO_2 - C_3H_7 + K_2CO_3 + C_2H_5OH.$$
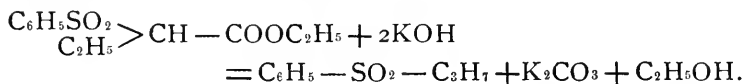
It does not appear possible to introduce ethyl into the monoethyl derivative, at least not by the method previously used. A solution containing sodium ethyl oxide, ethyl sulphone-ether and ethyl iodide, heated until it showed no alkalinity, gave nothing but unchanged ethylphenylsulphonacetic ether.

Action of allyl iodide on sodium phenylsulphonacetic ether.

The allyl derivative was prepared by heating an absolute alcoholic solution of ethyl sodium phenylsulphonacetate with allyl iodide until the solution became neutral. The new substance was precipitated from the alcoholic solution on addition of a sufficient quantity

of water, as an oil; and, after standing several hours, solidified to a crystalline mass. It was purified by several crystallisations from dilute alcohol, and was ethyl allylphenylsulphonacetate, as shown by the following sulphur estimation:

0.2882 gram of substance gave 0.2558 gram of $BaSO_4$.

$$\text{Theory for } \underset{C_6H_5SO_2}{\overset{C_3H_5}{>}}CH\text{-}COOC_2H_5. \qquad \text{Found.}$$

S   11.9   12.19

The compound crystallises from alcohol as rhombic prisms, melting at 64.5°. They are soluble in alcohol, ether and acetic acid, insoluble in boiling water.

The decomposition of ethylphenylsulphonacetate by alkalis into methylphenylsulphone and carbonate led us to expect the formation of allylphenylsulphone in the decomposition of the allyl derivative. An alcoholic solution of the compound and caustic potash was heated four hours at 120°, and, after inspissation, water and sufficient acid to neutralise the alkaline solution were added. The liquid was extracted several times with ether, and the ethereal solution deposited, on evaporation of the ether, long white crystals. These crystals may be crystallised from ligroin to which a few drops of alcohol are added; or better from acetic acid. The substance forms long prismatic needles, resembling those of phthalic anhydride. We were unable to obtain this substance in a state suitable for analysis, as it gradually changes into an amorphous compound; a change which takes place more rapidly the purer the substance.

Although a number of crystalline allyl compounds show a similar change to an amorphous state, it did not seem probable that allylphenylsulphone should show this property in so marked a degree; and we found by preparing that substance from allyl iodide and sodium phenylsulphinate that it is a heavy oil, which does not change on long standing. The sulphone adds bromine to form a crystalline substance. We intend to make these reactions the subject of further investigation.

Action of benzylchloride on ethyl sodium phenylsulphonebenzylacetate.

The endeavor to replace more than one hydrogen of phenylsulphonacetate by ethyl was not successful; but, on the other hand, the introduction of two benzyl takes place readily, yielding quantitative results.

The dibenzyl derivative was prepared by heating equivalent quantities of the sodium derivative of the monobenzyl compound with alcohol and benzylchloride to 100° for several hours. On evaporating the alcohol, the addition of water caused an oily substance to separate, which soon solidified, and was purified by crystallising from alcohol.

A sulphur analysis gave the following numbers:

0.2464 gram of substance gave 0.1390 gram of $BaSO_4$.

$$\text{Theory for } {}^{(C_6H_5CH_2)_2\!\!\diagdown}_{C_6H_5SO_2}\!\!>\!C-COOC_2H_5.$$

	Theory	Found.
S	7.8	7.75

Ethyl dibenzylphenylsulphonacetate crystallises from alcohol in white plates, melting at 118°. It is soluble in hot alcohol, moderately in cold; the insolubility of benzyl derivatives of phenylsulphonacetate increasing with the number of benzyl in the compound. The substance does not form a sodium derivative.

In a former paper[1] it was shown that benzylphenylsulphonacetate is decomposed by caustic alkalis into salts of phenylsulphinic and cinnamic acids; whereas the alkyl derivatives are decomposed by the same treatment into sulphones and carbonates. The dibenzyl compound undergoes the decomposition characteristic of the monobenzyl derivative, it yielding a benzylcinnamic acid.

Tubes containing three grams of the dibenzyl compound, five grams of caustic potash, and enough alcohol to dissolve them, were heated to 160° for six hours, and after the alcohol was driven off, acidified with sulphuric acid, and the product of the reaction extracted with ether. On evaporation of the ether a crystalline substance remained, which was purified by several crystallisations from acetic acid. The acid was analysed with the following results:

0.2935 gram of substance gave 0.8697 gram of CO_2 and 0.1767 gram of H_2O.

0.2346 gram of substance gave 0.6980 gram of CO_2 and 0.1432 gram of H_2O.

$$\text{Theory for } {}^{C_6H_5CH}_{C_6H_5CH_2}\!\!>\!C-COOH.$$

	Theory	Found.	
C	80.6	80.8	81.1
H	5.8	6.6	6.7

[1] This Journal **5**, 119.

Benzylcinnamic acid is found according to the following equation :

$$\begin{aligned}
&\overset{C_6H_5SO_2}{\underset{C_6H_5CH_2}{}}{>}CH-COOC_2H_5 + 2\,KOH = \\
&\qquad \overset{C_6H_5CH_2}{\underset{C_6H_5CH}{}}{>}C-COOK + C_6H_5SO_2K + C_2H_5OH + H_2O.
\end{aligned}$$
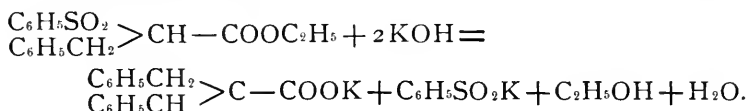
The acid forms large white needles, looking like those of phthalic anhydride, and melting at $157°$. It is insoluble in water and ligroin, easily soluble in alcohol, chloroform, ether, benzene and acetic acid when warm, moderately soluble in these liquids in the cold.

It dissolves readily in alkalis, forming soluble salts. The sodium salt was obtained by heating the acid with an amount of caustic soda insufficient to dissolve it, filtering and evaporating. It is a crystalline substance, and is very soluble in water. A sodium estimation gave as below :

0.1852 gram of salt, dried at $140°$, gave 0.534 gram of Na_2SO_4.

	Theory for $\overset{C_6H_5CH}{\underset{C_6H_5CH_2}{}}{>}C-COONa.$	Found.
Na	8.8	9.3

The silver salt is obtained by adding silver nitrate to the solution of the sodium salt, and consists of pearly rhombic plates that are but slightly soluble in cold water. Treated with nascent hydrogen benzylcinnamic acid takes up hydrogen, passing over into hydrobenzylcinnamic acid. An alkaline solution of the unsaturated acid was treated with sodiumamalgam until no further action was noticed, and the precipitate obtained by addition of an acid crystallised several times from dilute acetic acid. This compound was analysed with the following result :

0.3314 gram of substance gave 0.9758 gram of CO_2, and 0.2075 gram of H_2O.

	Theory for $(C_6H_5CH_2)_2CH-COOH.$	Found.
C	80.0	80.3
H	6.6	6.9

Dibenzylacetic, or hydrobenzylcinnamic, acid crystallises as tabular prisms, melting at $87°$. It is slightly soluble in hot water, very soluble in alcohol, acetic acid, benzene and chloroform. It dissolves its alkalis, forming salts. The addition of silver nitrate to a solution of the sodium salt gave the silver salt as rhombic prisms that are soluble in boiling water.

0.2238 gram of silver salt gave 0.0902 gram of AgCl.

	Theory for $(C_6H_5CH_2)_2COOAg$.	Found.
Ag	31.2	30.3

We had hoped to make use of the derivatives of phenylsulphon-acetic ether, to contribute to the question of the equal value of the four carbon affinities. Our experiments consisted in endeavoring to introduce benzyl into the ethylsulphone compound, and ethyl into the benzyl derivative; the object in view was to ascertain whether both these reactions would yield the same compound. The products of the action of ethyl iodide on benzyl-phenylsulphonacetate and benzylchloride on ethylphenylsulphon-acetate solidified only on long standing. We were unable to obtain from these products any other compounds in a pure state than the substances used as starting points.

Tufts College, Mass., *April* 3, 1885.

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NOTE ON THE CONSTITUTION OF THE ADDITION-PRODUCT OF CHLORHYDRIC ACID TO ETHYLCYANIDE.

By Arthur Michael and John F. Wing.

The nitriles of organic acids possess in a marked degree the property of uniting with halogens and halhydric acids, to form a series of interesting compounds, the constitution of which is still more a matter of conjecture than certainty. These compounds are sometimes classed as belonging to the so-called molecular compounds; again, as unstable chemical compounds. It is becoming more and more evident that a much greater degree of precaution is necessary in judging of the constitution of compounds belonging apparently to the same class, but either of a different series, or one whose radical has undergone a slight modification, than is at present customary. The replacement of a positive element like hydrogen by an atom of a negative element or negative group cannot fail to cause a readjustment of the affinities of the constituent atoms, and the atomic arrangement and stability of a

molecule may be dependent on such an interchange. Unless a thorough investigation of the two products is made, no great confidence can be given to a classification which places them in the same group.

The investigation of the compounds of halhydric acids with nitriles is of interest, as these compounds show properties which would seem to place them in the class of so-called double compounds. Again, they show properties which indicate a chemical union between the constituent substances. The compounds may be grouped into three classes, which are, considered as double compounds, $R-CNHCL$, $2R-CN,3HBr$, and $R-CN,2HBr$; as chemical compounds, the constitution $R-CClNH$ and $R-CCl_2-NH_2$ are adopted for the first and last, and we suggest $R-CBr{<}^{N-CBr-R}_{NH_3Br}$ for that of the middle class of compounds. The main reason for believing that they are chemical compounds is that they unite readily with water, forming ammonium salts and organic acids, under conditions of temperature that aqueous halhydric acids do not react on nitriles. But it must be remembered that, even if they are considered as double compounds, these are very different from a mixture of a nitrile and halhydric acid; besides that the former is soluble in water and, therefore, much more susceptible to its action, whereas the latter substances do not mix. It is evident that more cogent reasons must be sought for before the constitution of these compounds can be considered as definitely established; and, in the hope of contributing to this question, we have taken up the investigation of their behavior towards certain reagents.

The subject of the present note is the addition-product of chlorhydric acid to ethylcyanide, a substance that we prepared according to the directions of the discoverer.[1] The compound is probably the most stable of the compounds formed by the union of halhydric acids with nitriles; it may be crystallised from cold water without change, and also dissolves in alcohol without decomposition.

We have examined the action of sodium phenyl oxide and aniline on the compound, and have obtained results which are of value in judging the constitution of the substance. The nitrile compound, dried *in vacuo*, was dissolved in cold absolute alcohol, and somewhat less than the equivalent amount of aniline, also

[1] Gautier, Ann. de Chim. et Phys. [4] **17**, 184.

dissolved in alcohol, added. A reaction took place almost immediately and was shown by the solution becoming warm. In our experiments the solution was kept cold. The solution was allowed to stand several hours in a closed vessel, and then the alcohol evaporated by exposure to the air at ordinary room-temperature. The residue was dissolved in water, caustic soda added, and the alkaline liquid shaken out with ether. On evaporation of the ether an oil remained, which gradually, in two or three days, solidified. The substance was pressed between bibulous paper, and dried *in vacuo*. A nitrogen estimation gave the following result:

0.1587 gram of substance gave 27.8 cc. of nitrogen at 745 mm. and 26°.

	Theory for $C_9H_{12}N_2$.	Found.
N	18.92	19.04

The substance crystallises in rhombohedrons, melting at 68°. It is insoluble in water, soluble in alcohol and ether. Boiled with water it decomposes into ammonia and propio-anilide, melting at 116°.[1] Boiled with chlorhydric acid it is decomposed into aniline chlorhydrate and propionic acid.

The substance has basic properties. It dissolves readily in cold acids, and is precipitated as an oil by addition of alkalis. Platinum chloride added to a solution of the chlorhydrate gives gradually a yellow precipitate of the double platinum salt. This salt consists of radial groups of prisms with oblique end-faces. When allowed to stand for a long time with chlorhydric acid, or immediately when heated with the acid, it is decomposed with the formation of platinum ammonium chloride.

The analyses of the salt, dried at 100°, gave the following figures:

0.3391 gram of platinum salt gave 23 cc. of N at 750 mm. and 20°.

0.2568 gram of platinum salt gave 0.2897 gram of CO_2 and 0.0847 gram of H_2O.

	Theory for $(C_9H_{12}N_2HCl)_2PtCl_4$.	Found.
C	30.59	30.76
H	3.59	3.66
N	7.93	7.65

The base $C_9H_{12}N_2$ is formed from propionitrile by the addition of aniline, and agrees in its properties with those of an amidine. The

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[1] The melting point of this compound is given at 92° (Sestini, Zeitsch. chem. 1871, 35). The melting point of a product prepared from pure propionic acid and aniline was as stated above.

substance may be called propenylphenylamidine, and the formation of its chlorhydrate is represented by the following equation :

$$C_2H_5CClNH + NH_2C_6H_5 = C_2H_5 - C<^{NHC_6H_5HCl}_{NH}$$
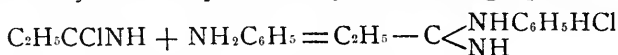
The action of sodium phenyl oxide on the addition-product gave less satisfactory results, although they are not altogether without interest. An alcoholic solution of the two compounds reacted in the cold, depositing sodium chloride, and the filtrate gave, on evaporation of the alcohol, a heavy oil, which did not solidify on standing, or at a low temperature. It is a base, as it dissolves in acids, and is precipitated from the solution by alkalis. The base is somewhat soluble in water, and the solution shows an alkaline reaction. We were unable to obtain it in a state suitable for analysis, and equally unsuccessful were the attempts to obtain its salts. A solution of the base in ether treated with dry chlorhydric acid gave an amorphous precipitate, which was doubtless the chlorhydrate, but the compound decomposed on standing into phenol and other products. The addition of platinum chloride to a chlorhydric acid solution of the base gave a precipitate of ammonium platinum chloride. The base is probably formed according to the following reaction :

$$C_2H_5CClNH + NaOC_6H_5 = C_2H_5 - C<^{OC_6H_5}_{NH} + NaCl.$$
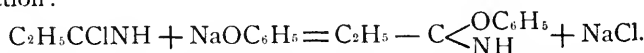
We believe that the above results prove the constitution of the addition-product of ethylcyanide and chlorhydric acid to a reasonable certainty. If the substance is considered as the molecular compound—$C_2H_5 - CN, HCl$—the first action of aniline would be to unite with the chlorhydric acid, setting free the nitrile ; the products of the reaction would be therefore aniline chlorhydrate and ethyl cyanide, and aniline chlorhydrate only acts on nitriles at a high temperature. The same reasoning applies to the action of sodium phenyl oxide ; in that case free phenol and ethyl cyanide should be formed. The formation of a basic product shows quite conclusively that in the compound in question chlorhydric acid must be in chemical combination with the nitrile. The constitution of the compound is therefore $C_2H_5 - CCl - NH$, and it may be called propenylchloro-imine or chlorpropylidene-imine. We intend to make this substance the subject of further experimentation, and also to examine the two other classes of addition-products of halhydric acids and nitriles in a similar manner.

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THE POST-MORTEM IMBIBITION OF ARSENIC.

BY FRANK S. SUTTON.

There is ample evidence that when arsenious oxide is introduced into the *living* organism it is absorbed and distributed, through the medium of the circulation, to all the tissues and organs of the body, and after death it may readily be recovered from any of these by appropriate chemical processes. It was thought, until very recently, that upon this fact rested a certain means of distinguishing between ante-mortem poisoning by arsenic and its introduction into the body after death, either for preservative purposes, or from motives less innocent; it being presumed in the latter instance that diffusion to the viscera outside of the alimentary canal would be prevented by the prompt conversion of any dissolved arsenic into insoluble sulphide by the gases of decomposition. This view is partly sustained by the undoubted fact that whenever arsenious oxide is thrown into the stomach or rectum of a dead body, the viscera in the immediate neighborhood are shortly found to be stained in varying degrees of intensity by yellow arsenic sulphide, and it is hence easy to account for the conviction long held by toxicologists that the presence of arsenic in the *viscera* of the body is proof of its ante-mortem administration. It remains to be seen, however, whether by subsequent oxidation of this sulphide to arsenic acid, or by solution in the ammoniacal liquids which decomposing nitrogeneous matters are so apt to give

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rise to, the means for extensive diffusion might not ultimately prevail.

Orfila was the first to give the subject scientific investigation, the results of his experiments being announced as early as 1839. These experiments, which consisted in post-mortem injections of arsenious oxide per mouth and rectum, both of the dog and the human subject,[1] demonstrated that in from one to three weeks, extensive diffusion to the viscera of the abdomen invariably occurred, and at numerous other places in the same work the author speaks of having established beyond doubt the fact of post-mortem diffusion to " all the organs of the body." It is to be noted, however, that nowhere, so far as the writer is aware, is the specific statement made that arsenic was either sought for or recovered from the *brain*. These early experiments of Orfila do not appear to have taken very strong hold among toxicologists, for the impression soon became current that the presence of arsenic in the *viscera* is demonstrative evidence of its introduction into the system during life, and it is only within a very recent period that this idea, so tenaciously held on to, has been forced out of sight.

In a paper read before the College of Physicians of Philadelphia, November 1, 1876, on the " Post-Mortem Imbibition of Poisons," Dr. Jno. J. Reese embodies a brief account of some experiments on this subject by Dr. Geo. Y. McCracken, as recorded in an inaugural thesis, presented to the Auxiliary Faculty of Medicine, University of Pennsylvania, June, 1876. The experiments with arsenic consisted in post-mortem injections into the stomachs of three dogs, and after burial for the respective periods of 21, 44 and 59 days, the principal viscera of the abdomen are stated to have contained arsenic, but the presence of the poison does not seem to have been looked for either in the viscera of the thorax or in the brain. The steps of the analytical process are not mentioned.

At a recent murder trial[2] in Michigan, the body of a lady who had died with symptoms of arsenical poisoning was exhumed 105 days after death, and, upon chemical analysis, Prof. Prescott found about 20 grains of arsenious oxide in the stomach and rectum together, and a small amount was also recovered from the liver ; at a subsequent period the body was again disinterred and the brain examined for arsenic, but none seems to have been found.

It being alleged at the trial that the husband had thrown arsenic to the amount of perhaps a teaspoonful into the mouth and rectum after death in order to preserve the body for removal, this fact gave rise to the query, " Granting that the arsenic was injected into the mouth and rectum in the manner claimed, could it reach the liver and other organs outside the alimentary canal?"   Upon this question the experts were equally divided, and in order to throw some light upon it. Drs. Vaughan and Dawson undertook a couple of experiments, one upon a musk-rat, the other upon the cadaver. In both instances, after injection per mouth and rectum with arsenious oxide suspended in water, and burial for 25 days, chemical analysis revealed arsenic in nearly all the organs of the body, and in both cases arsenic was found in the *brain.*   Commenting upon the comparatively large amount found in the brain of the musk-rat, the authors state that in the animal the bones of the skull are thin and not very firmly united ; and similarly, seeking an explanation of its presence in the brain of the human subject, the suggestion is offered that possibly owing to a regurgitation into the pharynx and nose, noticed during the process of injection, some of the arsenic adhered to the roofs of the passages and thence diffused into the cavity of the skull.

The chemicals used in the foregoing analyses are stated to have been proved free from arsenic.   The analytical method adopted consisted in destroying the tissues by potassium chlorate and hydrochloric acid, and from the ultimate product metallic mirrors were subsequently obtained by the modified Marsh apparatus of Chittenden and Donaldson.

In the same communication the authors embody the results of an experiment by Prof. Kedzie, of the Michigan Agricultural College, demonstrating diffusion of arsenic in the body of a cat, but no attempt seems to have been made to recover the poison from other than some of the abdominal and thoracic viscera.

Consideration of the foregoing experiments, which seem to be the only ones upon this subject of which there is any published record, leaves no room for doubt of the wide distribution of arsenic to the organs of the abdomen and thorax by cadaveric imbibition, both in the lower animals and in man, though we may question whether its presence in the heart and lungs is not to be accounted for on the assumption that part of the rejected fluid passed down the trachea.   The evidence of its diffusion to the brain is much less

satisfactory, as upon this aspect of the case Orfila is silent, while the only other testimony is conflicting. In the case of the human body examined by Prof. Prescott, 105 days after the alleged introduction of the arsenic, none seemed to have found its way into the contents of the skull, though the abdominal organs contained an abundance ; on the other hand, in the experiments of Drs. Vaughan and Dawson, where in both instances the time for diffusion was much shorter, the brain is stated to have contained appreciable quantities. This disparity, coupled with the fact that the affirmative testimony is somewhat weakened on account of the thin loose-jointed character of the bones of the skull in the musk-rat, and the regurgitation into the pharynx and nose in the case of the cadaver, serves to render the evidence of diffusion to the *brain* less positive and convincing than the importance of the subject in its medico-legal aspects would seem to demand. In the paper by Dr. Reese, already referred to, the author remarks that should it be proved as alleged by Scolosuboff, of Moscow,[1] that arsenic is deposited during life in the brain and cord, "we shall be in possession of a positive and unequivocal chemical method of distinguishing between ante-mortem and post-mortem poisoning by arsenic (and probably by other metals), by the detection of the poison in the brain and spinal cord, since it is scarcely conceivable that a poison introduced into a body after death could penetrate by imbibition within the cavity of the cranium or spinal column."

In view of these facts the following experiments were particularly directed towards determining the question of diffusion into the brain, and at the same time it was hoped to establish more definitely the shortest period during which general diffusion may be expected to take place. The subjects of these experiments were mongrel dogs, seven in number, as nearly uniform in weight as circumstances permitted. Death was produced by chloroforming, and in cases except where the conditions of the experiment called for a deviation, the aim was to inject 24 hours after death. The bodies were injected per mouth and rectum in accordance with the following uniform plan. The glottis being closed by a finger in order to avoid getting into the trachea, a straight glass tube was passed down the œsophagus into the stomach, and by means of a funnel attachment, 3 grams of arsenious oxide, diffused in about 50 cc. of water, were thus intro-

[1] Archives de Physiologie, No. 5, Août et Septembre, 1875.

duced. The same tube then sufficed to convey a like amount into the rectum, previously cleared as far as possible of its fæcal contents, but not more than 10 cc. of water were here found advisable, owing to the tendency to escape from the bowel. Thus injected, the bodies were buried under about 50 centimetres of soft earth for periods varying from 3 days to 3½ months, and then taken up for the removal of liver, kidneys and brain, and in one instance part of the spinal cord. Great care was taken to avoid contaminating any organ through the instruments used in removing preceding ones, and in no case was the alimentary canal cut into until all the desired viscera had been excised. In the experiments numbered V, VI and VII, where the periods of diffusion were shortest, and consequently the chances of arsenic reaching the brain at a minimum, the cranium was opened first, and its contents removed before cutting into the abdomen, so as to guard as fully as possible against accidental transfer from the one region to the other; and throughout the entire analysis each brain was examined in a separate fume closet, in order to still further avoid the possibility of contamination by extraneous sources.

The method of analysis was that recommended by Prof. Theo. G. Wormley[1] and in use at the laboratories of the Med. Dept., Univ. of Penna. Briefly, it consists in breaking up the tissues by potassium chlorate and hydrochloric acid, reduction by solution of sulphurous acid to condition of lower oxide, precipitation by a washed stream of sulphuretted hydrogen, solution of the precipitate in weak ammonia water, evaporation to dryness, repeated oxidation by strong nitric acid, followed by the addition of a few drops of strong solution of caustic potash with re-evaporation to dryness, and finally thorough charring by an excess of pure sulphuric acid; the latter is then completely expelled by heat, the pulverised carbonaceous mass extracted with acidulated water, and from the perfectly *colorless* filtrate the arsenic may be at once thrown down as magnesium ammonium arseniate, by rendering alkaline and adding magnesia mixture, or may be transferred to the Marsh apparatus; for Reinsch's test reduction by sulphurous acid is, of course, essential.

The purity of the reagents used in the foregoing process was proved for each in detail by Reinsch's test, excepting only the nitric acid, and collectively by the Marsh apparatus, by means of

[1] Micro-chemistry of Poisons, 2d edition, p. 301 *et seq.*

a blank experiment. Corroborative evidence of purity is also furnished by the fact that in Experiment No. VII the kidneys gave no trace of mirror whatever. It should be added that in those cases where Reinsch's test was employed, the presence of octahedral crystals was always demonstrated by the microscope. The only quantitative determination made was in the case of the liver of the dog longest buried, it being presumed from its size and position that this organ would contain the largest amount of arsenic, and the more in proportion as exposure to the influence of diffusion was protracted. In all cases the entire organs were used for the analysis. Following are the results in detail of the several experiments.

Experiment I.

Weight of dog, five and a half kilos; arsenic injected January 8, 1883, 23 hours after death; exhumed April 19, 1883. Length of interment, 102 days.

Post-Mortem Appearances.

Internal organs in good condition, appearing firm and natural, but brain very soft; a few dull yellow spots seen at sundry parts of the intestines; stomach half filled with a grayish pulp, but no yellow patches seen upon its walls.

The Liver.—Weight, 161 grams. One-fifth part of the final solution, representing one-fifth of the entire amount of arsenic recovered, easily responded to Reinsch's test, giving an abundant deposit on copper which was readily volatilised and condensed in octahedra. The arsenic in the remaining four-fifths was precipitated as magnesium ammonium arseniate, dried at 100° (C.) on an equipoised filter, and found to weigh 0.0153 gram. The whole amount recovered, then, was 0.019 gram, equivalent to 0.0099 gram arsenious oxide.

The Kidneys.—Weight = 42 grams. *One-tenth* part of the final solution gave prompt response, with octahedra, under Reinsch's test.

The Brain.—Weight = 51 grams. *One-fifth* part of the final solution tested with copper foil gave a perceptible steel gray coating from which octahedra were easily obtained. Verified by Marsh's test with part of the remaining four-fifths.

Experiment II.

Weight of dog, 5.2 kilos; arsenic injected February 5, 1883, twenty-six hours and a half after death; exhumed April 19, 1883. Length of interment, 74 days.

Post-Mortem Appearances.

Internal organs in good condition; bright yellow patches of various parts of intestines; stomach congested and showing one or two small yellow spots; empty, excepting a small bunch of grass.

The Liver.—Weight, 191 grams. *One-tenth* part of the final solution readily responded to Reinsch's test with production of octahedra.

The Kidneys.—Weight, 41 grams. *One-tenth* part of the final solution promptly coated copper from which octahedra were easily obtained.

The Brain.—Weight, 59 grams. *One-fifth* part of the final solution gave a good deposit on copper, and the resulting octa-hedra were readily made out. Verified presence of arsenic by Marsh's test.

Experiment III.

Weight of dog, 10.2 kilos; injected arsenic March 6, 1883, twenty-four and a half hours after death; exhumed April 19, 1883. Length of interment, 44 days.

Post-Mortem Appearances.

Internal organs well preserved; abundant yellow patches on rectum, colon and upper small intestines; stomach filled with food, congested in places, and with bright yellow spots on its anterior surface.

The Liver.—Weight, 300 grams. *One-tenth* part of the final solution gave heavy deposit on copper with subsequent octahedra.

The Kidneys.—Weight, 75 grams. *One-tenth* part of the final solution gave good deposit under Reinsch's test, but not so ready in coming down as in the liver solution.

The Brain.—Weight, 65 grams. *One-fifth* part of the final solution deposited on copper with difficulty and not very heavily;

yielded an invisible sublimate which showed under the micro-
scope merely as opaque dots. Presence of arsenic verified by
Marsh's test.

Experiment IV.

Weight of dog, five and a half kilos; arsenic injected April 1,
1883, 25 hours after death; exhumed April 19, 1883. Length of
interment, 18 days.

Post-Mortem Appearances.

Some dull yellow patches in rectum, and a faint yellow tint in
parts of the small intestine; stomach congested and empty, a few
yellow spots on its greater curvature.

The Liver.—Weight, 230 grams. *One-tenth* part of the final
solution promptly responded to Reinsch's test, octahedra being
readily obtained.

The Kidneys.—Weight, 48 grams. *One-tenth* part of the final
solution gave a less ready deposit than the liver solution; octahedra
easily recognised.

The Brain.—Weight, 41 grams. *One-fifth* part of the final
solution tarnished copper only when nearly evaporated to dryness;
the sublimate, as in the case of the brain in the previous experiment,
was not visible to the naked eye, and showed under the micro-
scope merely as a collection of opaque dots. Presence of arsenic
verified in the remainder by Marsh's test.

Experiment V.

Weight of dog, about 12 kilos; arsenic injected May 7, 1883,
6 hours after death, the body being quite cold; exhumed May 17,
1883; length of interment, 10 days.

Post-Mortem Appearances.

Abundant bright yellow patches in rectum and colon, the most
vivid yet seen; omentum also yellowish in places; stomach almost
empty, containing only a small amount of greenish liquid and a
little grass; deeply congested, as also the upper part of the
duodenum.

The Liver.—Weight, 417 grams. One-tenth part of the final
solution gave the usual prompt response to Reinsch's test,
octahedra being readily recognised.

The Kidneys.—Weight, 85 grams. One-tenth part of the final solution gave results similar to those of the corresponding liver solution.

The Brain.—Weight, 72 grams. Concentrated the *whole* of the final solution to a few cubic centimetres, and upon adding to a Marsh apparatus, a small but dense mirror speedily appeared.

Experiment VI.

Weight of dog, about 7 kilos; arsenic injected May 26, 1883, about 10 minutes after death, as near as could be determined; exhumed at the expiration of 3 days.

Post-Mortem Appearances.

Some few yellow spots in small intestines and parts of omentum; deep congestion of stomach, duodenum and liver; stomach empty; corrugations at cardiac end overlaid by an abundant collection of arsenious oxide; beneath this deposit appeared a few yellow specks.

The Liver.—Weight, 187 grams. One-tenth part of the final solution gave dense mirror in the Marsh apparatus.

The Kidneys.—Weight, 47 grams. One-tenth part of the final solution likewise gave a heavy mirror in Marsh's apparatus.

The Brain.—Weight, 63 grams. Concentrated final solution to about 1 cc. and upon throwing into a Marsh apparatus a small deposit shortly appeared, which was somewhat increased after 20 minutes, but which never amounted to more than a well-marked *stain.*

Experiment VII.

Weight of dog, 4½ kilos; arsenic injected June 2, 1883, 24 hours after death; exhumed at end of 3 days. In addition to the usual viscera, about 3 inches of the spinal cord were removed by sawing through the vertebral laminae in the middle dorsal region.

Post-Mortem Appearances.

Intensely yellow patches, by far the most vivid and abundant of any in the entire series, were noticeable in the region of the lower colon and rectum; stomach very full, most of the mass appearing

to be hair ; congested at cardiac end, and in the same region were found deep yellow spots on the mucous membrane. A lump of hardened fæces was noticed not far above the rectum, and lodged against it was a mass of arsenious oxide.

The Liver.—Weight, 147 grams. One-sixth part of the final solution gave a dense mirror in the Marsh apparatus ; the remaining five-sixths, reduced by sulphurous acid and subjected to Reinsch's test, coated but three small slips of copper, the arsenic then becoming exhausted.

The Kidneys.—Weight, 35 grams. The *whole* of the final solution, concentrated to a small bulk and thrown into Marsh's apparatus, gave no deposit whatever even after an interval of 15 minutes. This unlooked-for result may perhaps be explained by the presence of the impacted fæces in the lower bowel, already referred to, preventing ascent of the arsenic far enough up the intestine to reach the kidney in the short time allowed for diffusion, though it is not easy to understand why some should not have worked its way down from the stomach. Possibly position during burial, inclining the stomach in this or that direction, may have exerted an influence.

The Spinal Cord.—Weight, 3 grams. The final solution, concentrated to a small bulk and thrown into a Marsh apparatus, gave a faint deposit not perceptibly increased at the end of 15 minutes ; considering the small part tested, it is likely that the entire cord would have produced a distinct mirror.

The Brain.—Weight, 42 grams. Upon concentrating the final solution to a few drops and pouring into the Marsh apparatus, a barely visible *ring* shortly appeared, which did not seem to increase materially during the succeeding 15 or 20 minutes. This was the faintest deposit of the entire series.

The foregoing results may be tabulated as follows :

	I.	II.	III.	IV.	V.	VI.	VII.
Weight of Dog.	5½ kilos.	5.2 kilos.	10 2 kilos.	5½ kilos.	12 kilos.	7 kilos.	4½ kilos.
Time of Injection.	23 hrs. after death.	26½ hrs. after death.	24½ hrs. after death.	25 hrs. after death.	6 hrs. after death.	10 mins. after death.	24 hrs. after death.
Condition of Stomach.	Half-full of grayish pulp	Empty, except a little grass.	Filled with food.	Empty.	Almost empty; greenish liquid, and small bunch grass.	Empty.	Filled mainly with hair.
Length of Interment.	102 days.	74 days.	44 days.	18 days.	10 d. ys.	3 days.	3 days.
Liver.	Contained .0999 gram arsenious oxide; precip. and to Reinsch's test, weighed as Mag. Arseniate.	One-tenth final sol. promptly responded to Reinsch's test, giving octahedra.	One-tenth final sol. yielded heavy deposit on copper; octahedra easily obtained.	One-tenth final sol. readily gave octahedra under Reinsch's test.	One-tenth final sol. gave usual prompt response with octahedra, under Reinsch's test.	One-tenth final sol. gave dense mirror in the Marsh apparatus; remaining five-sixths under Reinsch's test coated but 3 slips of copper.	One-sixth final sol. gave dense mirror in the Marsh apparatus.
Kidneys.	One-tenth final sol. readily gave octahedra under Reinsch's test.	One-tenth final sol. under Reinsch's test, promptly gave octahedra.	One-tenth final sol. gave good deposit with octahedra, but not so ready in coming down as the corresponding liver solution.	One-tenth final sol. gave less ready deposit than the above liver solution; octahedra easily made out.	One-tenth final sol. gave good deposit; sublimate showed in Marsh's apparatus.	One-tenth final sol. gave a heavy mirror in Marsh's apparatus.	Final sol. concentrated and thrown into Marsh's app. gave no mirror after 15 mins.; arsenic absent.
Brain.	One-fifth final sol. gave octahedra under Reinsch's test; verified by Marsh's apparatus.	One-fifth final sol. responded to Reinsch's test, giving octahedra; verified by the Marsh apparatus.	One-fifth final sol. deposited with difficulty; sublimate invisible; appeared as minute opaque dots under the microscope; verified by Marsh's test.	One-fifth final sol. tarnished copper only when nearly evaporated to dryness; sublimate invisible, but shows under microscope as opaque spots, verified by the Marsh apparatus.	Final sol. concentrated to a few cc. gave a small but well marked stain in the Marsh apparatus, but no mirror.	Final sol. concentrated to 1 cc. gave a small but perceptible ring in the Marsh apparatus; but no mirror.	Final sol. concentrated to a few drops produced a barely perceptible ring in the Marsh apparatus; faintest of the entire series.
Spinal Cord.							Final sol. concentrated to small bulk, gave faint deposit in the Marsh apparatus; only 3 ins. of cord were used in this experiment.

On examining these results it will be noticed that while the brain of the dog buried ten days contained sufficient arsenic to give a small dense *mirror* in the Marsh apparatus, that from the brain of the dog buried three days, and in which the injection took place ten *minutes* after death, merely produced a well-marked *stain*, and, finally, in the brain of the dog buried three days but which had been injected 24 hours after death, the arsenic was present only in sufficient quantity to appear as an almost imperceptible *ring*. This successive gradation of intensity, occurring just as might be expected under the conditions of experimentation, granting that diffusion takes place at all, tends strongly towards showing that the presence of arsenic in the brain in these cases was not accidental, and that the amount contained, other things being equal, bears a direct ratio to the length of time for which diffusion was permitted to act. The experiment of injecting the poison shortly after death was undertaken in order to determine whether the greater fluidity and warmth of the parts would not favor a more rapid diffusion, and from the fact that a larger amount of arsenic was recovered from the brain in this case than in the experiment where the dog was injected 24 hours after death, the length of burial being the same in both cases, the question would seem to be answered in the affirmative.

It is of interest to know by what route the arsenic reached the brain, but the facts at command do not warrant a definite conclusion. It is not very likely that in so short a period as three days general diffusion through the tissues and entrance into the cranium through the foramen magnum would have taken place, but there are two or three other avenues worthy of attention which are more promising. The intestines being richly supplied with lymphatics, all leading to the thoracic duct, and this in turn emptying into the subclavian vein at the base of the neck, a possible route here suggests itself; a more roundabout way would be through the portal system to the heart and thence up the superior vena cava; at autopsies and in the dissecting-room we generally find the blood in the veins more or less fluid, doubtless through the breaking down of the primary coagulum, and thus the routes here sketched are among the possibilities. On the other hand, the presence of arsenic in the spinal cord, as evidenced in Experiment VII, and which in fact was there sought with no other object than to locate the channel through which the arsenic reached the brain, affords

good grounds for the belief that part, at least, finds access to the cranial cavity through the medium of its continuation in the spinal column. It will be remembered that the sub-arachnoid space is filled with fluid, continuous with a similar fluid in the brain, and thus, having diffused through the tissues about the vertebral column and reached this space, an easy channel to the brain is afforded.

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A METHOD OF FILTRATION BY MEANS OF EASILY SOLUBLE AND EASILY VOLATILE FILTERS.

BY F. A. GOOCH.

The processes of analysis, in which it is desirable to redissolve precipitates from the filter after washing, or to separate a mixed precipitate into parts by the action of appropriate solvents, are many.

When a complete solution is the object, and the precipitate yields easily to solvents which do not affect paper injuriously, the use of the ordinary filter offers no difficulty. When, however, precipitates are to be treated with reagents which disintegrate paper filters, the case is otherwise; and the attempt to remove, by solvents, any individual part of a mixed heterogeneous mass upon a filter is always an uncertain matter. As examples of cases of this sort, difficult to deal with, we may take the solution of acid sodic titanate in strong hydrochloric acid; or the purification of baric sulphate from included salts by digestion in strong hydrochloric acid; or the separation of sulphides which are soluble from those which are insoluble in alkaline sulphides; or the washing out of free sulphur from precipitated sulphides by means of carbon disulphide; or the separation of calcic and baric sulphates by the action of sodium hyposulphite. In cases of this nature it is often convenient to make use of the asbestos filter which I have previously described;[1] but this sometimes has its

[1] This Journal **1**, 237.

disadvantages.   Thus, to recur to the examples just cited, acid
sodium titanate may be filtered and washed upon an asbestos filter,
and felt and precipitate treated together with hydrochloric acid,
but it will be impossible to determine when solution is effected
because of the floating asbestos ; and in separating the sulphides
it would be necessary to know the weight of the asbestos felt, since
it must be weighed finally with the insoluble sulphides, unless
removed by a special treatment which involves the solution,
filtration and reprecipitation of the latter.

It is to meet cases like these that I have sought a filter which, in
the reversal of the ordinary mode of separating filter and pre-
cipitate, should dissolve easily in solvents which do not affect the
ordinary precipitates met with in analysis.   The material which
seems best suited to the case—light and fluffy, capable of making
secure filters of any desirable degree of porosity, sufficiently
insoluble in water and aqueous solution of salts, alkalies and acids
(excepting strong sulphuric, strong nitric, and glacial acetic acids),
easily soluble in naphtha, benzol, carbon disulphide, ether, boiling
alcohol, and essential oils, and not too costly—is anthracene.

The mode of preparing and using the filter is simple.   Anthracene
is slightly moistened with alcohol to make it miscible with water,
diluted to the right consistency, and applied to the same apparatus,
and in the same way, as the emulsion of asbestos which is employed
in making asbestos felts.   That is to say, enough of the emulsion
in water to form a layer of the proper thickness is poured into a
perforated crucible which is held tightly in a packing of rubber
tubing stretched over a funnel fitted in the usual manner to a
vacuum-flask or receiver.   After washing with water the filter is
ready for use.   If the felt happens to be too coarse for the use of
the moment, it may be made as close as need be by coating the
felt first deposited with a finer emulsion, made by dissolving
anthracene in hot alcohol and precipitating with water.   When
voluminous precipitates are to be filtered, the large perforated
cone described in the former paper, to which I have referred,
may be substituted with advantage for the crucible ; or Cooke's
improved form [1] of Carmichael's process of reverse filtration may
prove most useful.   In using the cone it is well to apply the
anthracene in a thick layer.

To remove the anthracene filter from a precipitate it is only

[1] Proceedings of the American Academy **12**, 124.

necessary to act with the proper solvent.   It is usually convenient
to stand the crucible containing precipitate and felt in a small
beaker, add enough of the solvent, and gently warm until the
anthracene dissolves.   On the addition of water, or the reagent to
work upon the precipitate, the solution of anthracene floats, and
nothing remains to obstruct or obscure the action.   If the pre-
cipitate dissolves entirely, the solution of anthracene may be
separated from the aqueous solution by simply pouring the fluid
upon a filter previously moistened with water, when the solution
in water runs through, and the anthracene and its solvent remain
and may be washed indefinitely with water.

   If, on the other hand, the case is one of the division of precipi-
tates, the anthracene and its solvent may be made to pass the filter,
after the water has run through, by adding a little alcohol to over-
come the repulsion between the solution and the water which fills
the pores of the filter, the precipitate which stays behind being
washed first with a solvent of anthracene, and then, if necessary,
with alcohol followed by water; or, if the vacuum filter be used
(either paper or asbestos, according to the circumstances of the
case), both liquids leave the precipitate and traverse the filter
together.

   In general I prefer benzol as the solvent for anthracene, but
some advantage may be gained in special cases by a proper choice
of solvents.   Thus, in removing intermixed sulphur from precipi-
tated sulphides, both the anthracene and the sulphur may be dis-
solved in carbon disulphide in a single operation.

   The ready volatility of anthracene, at a temperature very near
its melting point, 213° C., makes it easily separable in cases when
to remove it by a solvent is not advisable.   The treatment of a
solution of anthracene, for example, with strong sulphuric or nitric
acid is apt to produce carbonaceous or gummy residues.   In such
cases it is well either to heat precipitate and filter directly, or to
first remove them from the crucible by means of a solvent for
anthracene, then evaporate this and raise the heat gently until
the anthracene has vanished.   The purification of precipitated
baric sulphate, by dissolving it in hot, strong sulphuric acid, and
reprecipitating by dilution, is a case in point; and one, too, in
which the reversed filter may be used with great advantage.   It
may be remarked, in passing, that if one does not happen to
possess a platinum rose, and does happen to have at disposal a

perforated crucible, a very fair reversed filter may be improvised of the crucible, a piece of glass tubing, and a rubber stopper, the last being fitted to the crucible, and the tube passed through nearly to the perforated bottom.

At every point in the preparation and use of the anthracene filter I have found the manipulation peculiarly easy.

ELECTROLYSIS OF MOLYBDENUM SOLUTIONS.

By Edgar F. Smith and W. S. Hoskinson.

In a paper published by one of us (S.) in Vol. I, No. 5, of this Journal, attention was directed to the action of the electric current upon alkaline molybdic acid solutions. We there showed that although this method of precipitation was complete, yet the unusual time (100 hours) required rendered it practically useless. Since then we have found that by employing neutral solutions or such as contain a very slight excess of sulphuric acid, quite satisfactory results can be obtained.

The form in which the molybdenum separates on the crucible sides is as black $Mo_2O_33H_2O$, as already observed (Vol. I, No. 5). When the precipitation is complete the liquid is carefully siphoned off, the bright, compact coating washed with water, and the crucible with its deposit dried upon a water bath (about 90°) and weighed. It may be well to carefully ignite the black oxide in a covered crucible and thus convert it into trioxide, and weigh in the latter form.

In Volume 4 of the *Handwörterbuch der Chemie* it is stated that the electric current precipitates metallic molybdenum from solutions of ammonium molybdate. The determinations made by us under varying conditions do not confirm this statement. Our product in all instances was $Mo_2O_33H_2O$.

For our experiments we employed solutions containing different amounts of molybdenum. The precipitation was made in a platinum crucible of about 30 cc. capacity, although the dilution rarely exceeded 25 cc., so that space remained for exposure of fresh surface, and in this way afforded a ready means of knowing when

the precipitation was complete. The filtrate and washings from the deposit were always examined for molybdenum. The deposition of oxide occurs upon the zinc pole of the battery.

EXPERIMENTS.

I. In a solution containing .0093 gram molybdenum as ammonium molybdate we obtained by electrolysis:

	$Mo_2O_3 . 3H_2O.$	Mo.
1.	.0146 gram.	.0095 gram.
2.	.0146	.0095
3.	.0138	.0090
4.	.0137	.0089
5.	.0138	.0090
6.	.0142	.0092
7.	.0143	.0093
8.	.0146	.0095
9.	.0146	.0095
10.	.0146	.0095

Molybdenum was not found in the filtrate. The time required for the above precipitations was two hours in each case. The current was obtained from four small-size Grove cells.

II. The solution contained .0156 gram of molybdenum. We obtained:

	$Mo_2O_3 . 3H_2O.$	Mo.
11.	.0236 gram.	.0154 gram.
12.	.0239	.0156
13.	.0245	.0160
14.	.0228	.0148

The time of precipitation was two hours. Used four Grove cells. No indications of molybdenum in any of the solutions after the deposition of oxide.

III. A solution containing .0167 gram molybdenum gave:

	$Mo_2O_3 . 3H_2O.$	Mo.
15.	.0256 gram.	.0167 gram.
16.	.0252	.0164
17.	.0258	.0168
18.	.0258	.0168
19.	.0257	.0166

Three hours were employed in precipitating the above quantities. Four Grove cells. Molybdenum not found on testing the filtrates.

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IV. We found in a solution containing an unknown amount of molybdenum :

	$Mo_2O_3 . 3H_2O.$
20.	.0325 gram.
21.	.0329
22.	.0330
23.	.0315

The time was three hours. Employed the same battery power as in the other determinations ; 23 is the only instance where molybdenum was detected.

The action of the current upon molybdenum solutions containing other metals is receiving study at present.

WITTENBERG COLLEGE, O., *April* 7, 1885.

ON THE DETECTION OF ADULTERATIONS IN OILS.

BY OSCAR C. S. CARTER.

The chemical examination of oils is a very important though much neglected study—important from the fact that the oils which command a high price in the market and are in general demand are frequently adulterated. The temptation to adulterate is great on account of the heavy increase in profit, and because the adulterant is often very difficult of detection. The purchaser is always at the mercy of the oil merchant, unless the oil be submitted to a chemical examination. " Our former Consul at Naples reported to the State Department that immense quantities of refined cotton seed oils are sent to Italy for the express purpose of sophisticating the native olive oil, for the reason that it can be brought to Naples and sold at less than half the cost of producing pure olive oil." The cotton seed oil mixed with pure olive oil is exported to other countries. The price of fine salad oil is from three to four dollars per gallon, while cotton seed oil is worth from seventy to ninety cents per gallon. The oils commonly used to adulterate olive oil are colza oil, sesame oil and peanut oil. In the North of France poppy oil is used frequently because of its cheapness and neutral taste, and in Provence honey is used. In all probability glucose

syrup has been tried.   Linseed oil, the most important drying oil
in the arts, so much used in varnishes and paints, is very often
sophisticated.   Even the seed from which the oil is made is mixed
with other seeds.   In India flaxseed is grown with mustard and
rape.   In Russia various proportions of hemp and linseed are sown
together.   Hemp seed yields an oil of an acrid odor, mild taste
and yellow color, used in Russia for burning in lamps and making
paints, varnishes and soap.   The oils commonly mixed with linseed
oil are niger, cotton seed, fish, rosin and coal oils.   In this country
lard is adulterated with palmnut and cocoanut oil; the latter is a
white fat with the peculiar smell of the kernel.   It was formerly
made by grinding the kernel, boiling with water and subjecting the
paste to a great pressure ; a large quantity of milky juice is so
obtained, which is slowly boiled and the oil separates and is skimmed
off.   Twenty ordinary sized nuts yield about two quarts of oil.
The strong taste of these oils is an objection, and may prevent their
general use as adulterants and for the manufacture of oleomarga-
rine.   Lard oil, which is obtained from lard, is very valuable as a
lubricant for machinery, and is also used for greasing wool in
spinning.   It is frequently adulterated with fish oils and cotton
seed oils.   Lard oil is worth one dollar and twenty cents per
gallon, while cotton seed oil is worth about one-half as much.

The chemical analysis and detection of the adulterated oil is
sometimes simple, but generally it is a difficult and trying task,
especially when three or more oils have been mixed.   The deter-
mination of the percentage of oil used to adulterate is out of the
question, and we must often be satisfied by simply proving that
there has been a mixture without knowing the nature of it.   But
little work has been done on oils compared to the vast amount of
research given to other subjects.   Chemists have avoided the
study and analysis of oils as difficult and uninteresting.   We owe
almost all we know to the labors of Chevreul, and later to the
researches of Prof. Allen and others.   When oils are examined,
chemical tests are the more important, but the physical tests are
also very useful.   At the present time we have not a characteristic
test for each oil, as we have for each metal, that will distinguish it
when mixed with other oils or that will identify it when alone.

When we examine an oil supposed to be adulterated, much can
be accomplished by procuring a sample of perfectly pure oil and
subjecting them both to the same tests and observing their behavior.

A sample of lard oil supposed to be adulterated was received from a woollen manufacturer for examination. A specimen of perfectly pure lard oil was obtained and they were subjected to the same tests.

According to Professor Bechi, of Florence, the following test is reliable and delicate for detecting cotton seed oil in olive oil. The reagent is a one per cent. solution of nitrate of silver in absolute alcohol. Place 5 cc. of the suspected oil in a glass flask, add to it 25 cc. of absolute alcohol and 5 cc. of the test solution of nitrate of silver, made as stated above. The flask is heated in a water bath at 84° C. (direct heat must not be used). If there be any cotton seed oil present, the mixture will begin to darken, the most minute quantity serving to discolor, and the tint assumed will depend upon the amount of cotton seed oil present. The test depends upon the fact that cotton seed oil will reduce nitrate of silver, but olive oil will not. This reduction is also caused by rape seed oil, but according to Bechi, pure olive oil will remain without discoloration under this test. While experimenting with the test I thought it might be of service in detecting cotton seed oil in lard oil; accordingly the sample of chemically pure lard oil was treated with absolute alcohol and nitrate of silver as directed and then heated; there was not the slightest discoloration of the pure lard oil; even on standing for two weeks it did not darken, thus proving it had no action upon the nitrate of silver. The lard oil obtained from the woollen manufacturer was then tested in the same manner; when it had been heated for a few minutes it began to darken and finally became quite black, thus proving that the lard oil was not pure, but mixed with some other oil. I am not certain that the darkening is due to reduction; having made a series of experiments with salts of mercury, copper, and antimony and cotton seed oil to see if there would be any reduction I obtained no satisfactory results, and no reduction was noticed.

The elaidin test is sometimes very satisfactory, especially in detecting a mixture of a drying and non-drying oil and detecting adulteration of olive oil. This test depends upon the fact that olein and oleic acid in contact with peroxide of nitrogen yield a crystalline, solid, fatty body fusible at 32° C. to which Boudet has given the name elaidin. The nitrous vapors made by the action of nitric acid on copper are passed through the oil, or it may be shaken with a fresh solution of mercurous nitrate which has the

property of retaining nitrous acid.   Non-drying vegetable oils and
most animal fats contain oleic acid.   The following oils contain a
high percentage of olein : olive, almond, rape, arachis (earthnut),
castor, and the oils from lard and tallow.   These oils form with
nitrogen peroxide solid elaidin of a white or yellow color, which in
some cases is firm and resonant.   The drying oils, such as linseed,
hemp seed and poppy seed oils, do not form solid elaidin with
nitrous vapors, but remain liquid for more than two days and
become slightly colored.   The elaidin test was applied to the
adulterated lard oil and to the pure lard oil by adding an equal
amount of nitric acid (sp. gr. 1.40) and some copper turnings.
The elaidin produced by the pure oil was more firm and coherent
than that of the adulterated oil and was of a lighter color ; also
the nitrous fumes rose more rapidly through the pure oil.   One
curious fact noticed about the adulterated lard oil was, it could not
be completely saponified with caustic soda ; even when the latter
was added in excess, a clear layer of unsaponified oil remained
after several trials.   This test clearly indicated adulteration, as
pure lard oil will completely saponify with caustic soda.   Prof.
Allen has proved that shark liver oil and African fish oil resist
saponification.   He tried to saponify the former oil with aqueous
potash, with a solution of potash in absolute alcohol, and by heat-
ing it with solid potash, but it would not completely saponify ; this
he thinks is due to the fact that it contains a body allied to choles-
terin, but fluid at ordinary temperatures.

Pure lard oil gives with nitric acid of sp. gr. 1.33 a yellow color,
approaching orange.

The adulterated sample of lard oil with nitric acid of the same
strength gave a distinct brown color on standing.   That portion
of the oil which resisted saponification with caustic soda was treated
with nitric acid, and it soon became of a deep coffee-brown color,
much darker than the above.

The determination of specific gravity is the most important of
the physical tests.   The viscosity of an oil is a highly important
feature, but in order to be of any value in testing, much care must
be observed ; both oils must be brought to the same temperature,
and kept so while flowing.   Both the adulterated and the pure
lard oil were subjected to this test; they were brought to a temper-
ature of 80° F., and 5 cc. of each oil were passed through a capil-
lary tube.   The pure oil required 960 seconds to pass through,

while the adulterated oil required 1080 seconds. The experiment was repeated several times with different tubes, but the ratio of the times of flowing was constant. Both oils were subjected to a temperature of 32° F. When the pure oil was frozen it was more coherent and firm and much lighter in color ; the adulterated sample was quite yellow. When the adulterated oil slowly became liquid a layer of yellow oil formed first, which was quite different in appearance from the other portion and was evidently the adulterant.

While we cannot depend on any single test, the evidence afforded by several is often conclusive and satisfactory, and in this case it was acknowledged afterwards that cotton seed oil was one of the adulterants.

Central High School, Phila.

ON THE UNIT USED IN CALCULATING THE ATOMIC WEIGHTS.[1]

By Lothar Meyer and Karl Seubert.

The controversy arising immediately after the proposal of Dalton's atomic theory, as to the unit upon which the numerical values of the atomic weights should be based, has for a half-century divided chemists into two schools. While Dalton and, later, Leopold Gmelin, from theoretical and philosophical considerations, chose the smallest atomic weight, that of hydrogen, as the measure of all the rest, Wollaston and Berzelius chose that of oxygen, partly because they did not place so high a value on theoretical views, partly and especially on the purely practical ground that many elements can be compared directly with oxygen, whereas they can be only indirectly compared with hydrogen. When the Dalton unit, the hydrogen atom, gradually obtained the upper hand, the old controversy appeared to have been laid aside, and consequently it was to be hoped that the recent more exact investigations of the laws which govern the numerical values of the atomic weights would be directed from the same point of view.

This hope, however, has unfortunately not been fulfilled, as the old Wollaston-Berzelius unit has lately again come into use in a different and, as we believe, more dangerous form.

As is well known, J. S. Stas[1] has, from his own observations as well as those of others, deduced as the most highly probable result, that the atomic weight of oxygen is not quite sixteen times as great as that of hydrogen, but on the contrary is about $\frac{1}{400}$ of its value less than 16H. This follows :

(1) From the numerous gas analyses (reduced to weight) conducted since the discovery of Gay Lussac and von Humboldt, or, what amounts to the same thing, from Avogadro's law and the experimentally determined densities of both gases (No. 1 a,[2] and Julius Thomsen, Berichte der deutschen chemischen Gesellschaft, 3, 927) ;

(2) From the synthesis of water by means of copper oxide (*loc. cit.* No. 1 c, d) ;

(3) From the relations of sal ammoniac to silver nitrate and of both to silver (*ib.* No. 47 and 83), where, as confirmatory of the atomic weight of nitrogen (N = 0.877910) used in the calculations, the relations of the chlorides and metals to the nitrates could also be determined (No. 131, 132, 133, 135); and further, though with somewhat less certainty,

(4) From the relation of the crystallised and dehydrated strontium chlorides to each other and to silver (No. 65 c and 140) ;

(5) From the relation of these substances to each other and to the sulphate (No. 197) ;

(6) From the corresponding numbers for crystallised and dehydrated barium chloride and silver (No. 66 e and 141) ;

(7) From the relation of both forms of barium chloride to the sulphate (No. 188 d) ;

(8) From the relation of aluminium to hydrogen and to water (No. 8 c, d and 144).

The determinations deduced from methods 1 and 2, undoubtedly the most exact, give as a mean the ratio

$$H : O = 0.06265 : 1 = 1 : 15.96$$

which Stas considered as coming nearest to the truth. The simple ratio of 1 to 16 demanded by Prout's hypothesis in one

[1] Nouvelles recherches sur les lois des proportions chimiques. Bruxelles, 1865, p. 24, etc.

[2] Die Atomgewichte der Elemente aus den Originalzahlen neu berechnet, von L. Meyer und K. Seubert. Leipzig, 1883.

sense lies entirely outside of the observed values, in another sense very near to their extreme limits. To an unprejudiced judge not biassed in favor of that hypothesis, not yet established by the best observations, there appears no ground for accepting this numerical relation rather than that obtained as the mean value.

Further, if the simpler ratio be accepted, the experiments embraced under the heads from 3 to 8 yield results almost all of which agree less well than if the more complex ratios were accepted, and the differences between the calculated values and those obtained under 3 are greater than could be accounted for on the supposition that they are due to errors of observation.

But since this relation between the atomic weights of hydrogen and oxygen had not yet been as accurately determined as that of other elements to one another, Stas, in order to show the utter indefensibility of Prout's hypothesis, calculated all the atomic weights determined by him upon the assumption, *incorrect according to his opinion*, that the atomic weight of oxygen is just sixteen times as great as that of hydrogen. He pointed out that even with this assumption Prout's hypothesis would not hold good for the rest of the atomic weights under investigation. This supposition, made by Stas merely for the sake of argument, appears to have been much misunderstood ; as if the value $O = 15.96$ and $O = 16.00$ were exactly the same, which of course is not at all the case. It is rather in a high degree probable, if not certain, that the number 16 is incorrect to 3 or 5 units in the second decimal place, whereas the other value 15.99 is out only 1 or, at the most, not more than 2 units.

Since we were at that time accustomed to reckon with $O = 16$, and Stas naturally discussed only those atomic weights which had been newly determined by him, the choice was offered whether to calculate all atomic weights with the corrected values of oxygen, silver, chlorine, etc., as a basis, or provisionally to manage further with the old numbers, and merely introduce the corrected atomic weights of Stas into a system resting upon a somewhat more defective basis. This last, incorrect indeed, but more convenient way, was chosen by many chemists. This could the more easily be done since most of the atomic weights in use at that time were justly looked upon as not being very accurate, and a difference of $\frac{1}{400}$ of a value was of very little practical consideration.

The hope that at least the old controversy over the choice of

the unit would disappear upon a recalculation of the atomic
weights of all the elements, has unfortunately not been fulfilled.
There is a universal desire to do away with the unit preferred by
Thomsen, Wollaston and Berzelius,

$$O = 1, = 10 \text{ or } = 100,$$

and to refer all atomic weights to hydrogen. But as to the way
in which this should be done, opinions differ. With a few
exceptions (as in the case of Al, No. 8 c, d), the relation to
hydrogen is deduced only through the intervention of oxygen,
consequently the numerical values of all atomic weights depend
upon that of oxygen. In consideration of this we have, in our
recalculation of the atomic weights referred to above, made use
of the Wollaston-Berzelius unit ($O = 1$), as well as the usual one
($H = 1$), so that in case of a new, more trustworthy determination
of the relation $O : H$, the numbers referred to hydrogen as 1 could
easily be corrected. A few years earlier G. F. Becker[1] referred
all the atomic weights to $O = 16$. F. W. Clarke[2] has, like us,
taken $H = 1$, but has also, out of fondness for Prout's hypothesis,
given a table in which $O = 16$ and consequently $H = 1.0023$.
J. Sebelin[3] makes use of the same units as we do ($H = 1$ and
$O = 100$), and only occasionally adds a few numbers calculated
on the supposition that $O = 16$. W. Ostwald[4] does not agree
with Stas that the value $O = 16$ is too large, but thinks that, from
the last five observations of Erdmann and Marchand,[5] the first
three of which he casts aside, it must follow that for $H = 1$,
O must be exactly 16.00, though the sum of all the experi-
ments of these authors gives $O = 15.96$. J. D. van der Plaats[6]
inclines to the view that O may be equal to 16, though he con-
siders the question as still open. W. Dittmar[7] has recalculated
the atomic weights, calculated by us on the basis $H = 1$, on the
basis $O = 16$ and $H = 1.0024$.

In consequence of these different views, all the other atomic
weights fluctuate to the extent of about $\frac{1}{4}$ per cent. of their value,

[1] Atomic Weight Determinations; a digest of the investigations published since 1814.
Washington, Smithsonian Institution, 1880.

[2] A Recalculation of the Atomic Weights. Washington, Smithsonian Inst. 1882.

[3] Beiträge zur Geschichte der Atomgewichte. Preisschrift, Braunschweig, 1884.

[4] Lehrbuch der allgemeinen Chemie. Leipzig, 1884.

[5] Meyer and Seubert, No. 1 d ; Clarke, p. 5.

[6] Comptes Rendus, Jan. 5, 1885, 100.

[7] Tables to facilitate chemical calculations. 2d Ed. Glasgow, 1885.

amounting in the case of the largest to one-half of the unit. That such a condition of things is undesirable, all scientific men are agreed, and also, that the very smallness of the difference aids in the confusion and perplexity, since every author will not state, in every article, the standard according to which he calculates.

How the evil is to be remedied is difficult to say. First of all it is to be remembered that both values for the atomic weight of oxygen lie within the limits of errors of observation, and that, in case authenticated constant errors tend to lower the result, it may even be admissible to take the maximum value $O = 16.03$ instead of the mean value $O = 15.96$. It is more questionable, however, to round off this maximum value just at the number 16, for which there are no grounds except the unproven Prout's hypothesis. The secret or confessed fondness for this hypothesis is probably the true cause of the choice of this number. We willingly acknowledge that there may be concealed in this hypothesis of Prout's a valuable idea; but this does not change the fact that, *as now stated, the hypothesis is untenable.* Wherever up to this time the proof has been looked into with sufficient exactness, it has shown that the atomic weights are not exact multiples of whole numbers, and this result is independent of the relation of oxygen to hydrogen. Accept this or not as we will, we always obtain for the atomic weights, when most accurately determined, irrational numbers.

What seems to be most noteworthy in Prout's hypothesis is brought into view, and in an unprejudiced manner, when we take the relation of H : O as given by the most accurate observations. For instance, it is a striking fact that the atomic weights of more than one-fourth of all the elements are very nearly multiples of the half atomic, or equivalent weight of oxygen, as the following table will show.

Multiples of $\frac{1}{2}$ O $=$ 7.98.

Factor.	Product.	Atomic Weights.	Difference.
1	7.98	...	...
2	15.96	O $=$ 15.96	o
3	23.94	Mg $=$ 23.94	o
4	31.92	S $=$ 31.98	$+$ o o6
5	39.90	Ca $=$ 39.91	$+$ 0.01
6	47.88	Ti $=$ 48.01	$+$ 0.13
7	55.86	Fe $=$ 55.88	$+$ 0.02
8	63.84	(Cu $=$ 63.18)	($-$ 0.66)
9	71.82	Ekasilicon.	...
10	79.80	Br $=$ 79.76	$-$ 0.04
11	87.78	(Sr $=$ 87.3)	($-$ 0.48)
12	95.76	Mo $=$ 95.9	$+$ 0.14
13	103.74	Ru $=$ 103.5	$-$ 0.24
14	111.72	Cd $=$ 111.7	o
15	119.70	Sb $=$ 119.6	$-$ 0.10
16	127.68	...	...
17	135.66	...	...
18	143.64	Di $=$?	...
19	151.62	Break in VI.	...
20	159.60	...	...
21	167.58	Eb $=$?	...
22	175.56	Break in IV.	...
23	183.54	W $=$ 183.6	$+$ 0.06
24	191.52	Os $=$?	...
25	199.50	Hg $=$ 199.8	$+$ 0.3
26	207.48	Bi $=$ 207.3	$-$ 0.18
27	215.46	...	...
28	223.44	...	...
29	231.42	Th $=$ 231.96	$+$ 0.54
30	239.40	U $=$ 239.8	$+$ 0.4

Such regularities are worthy of note ; but to attempt to correct the atomic weights by them would be just as incorrect as to round them off into whole numbers.

He who does not adhere to Prout's hypothesis, and is besides not of the opinion that the observations yield as the most probable value of the relation O : H $=$ 16 : 1, has, according to our view, not the least ground for giving the value O $=$ 16 the preference over O $=$ 15.96. Then, if we take the atomic weight of oxygen, not as $=$ 1 or $=$ 10 or $=$ 100, but as $=$ 16, the only meaning that can be attached to it is, that it appears more proper to take the hydrogen atom as the unit. This view is universally held ; but since its relation to oxygen is uncertain to a few thousandths of its value, it is thought that the round number 16 may be used instead of the 15.96 found, though it is necessary in this case to place H $=$ 1.0025, *i. e.* to take as the unit $\frac{399}{400}$ of the

atomic weight of hydrogen. Such a wonderful unit can only be endured in the quiet hope of the future fulfilment of the hypothesis of Prout. In the end hardly any one will seriously wish science to be burdened with it.

It is admitted that with the atomic weight of oxygen uncertain, all others remain so likewise in the fourth and following places of their numerical values, while their relative values, their relations to one another, in many cases are correctly determined to the fourth, and in some cases even to the fifth place. These facts can be changed by no hypothetical considerations. If to-morrow the relation O : H should be determined more accurately to the one or two thousandth part of its value, and this number should differ from the one accepted to-day, all the other atomic weights would have to be recalculated.

What advantage is offered in calculating with $H = 1.0025$ and $O = 16$ we cannot possibly see. The fact that the numerical values for oxygen, carbon and a few other elements are thereby reduced to two figures, can hardly appear so desirable that one should, for this reason, consent to the choice of such a nonsensical unit.

It has been stated that the error which would be introduced by making $H = 1$ is much smaller than the unavoidable errors of observation.

But so far as this is concerned, it may on the other hand be asked : Why introduce even so small an error when it can be avoided ? Our observations are, without this, already sufficiently subject to sources of errors of all kinds. It does not change the case at all if the omission of these small fractions does *not* influence the decimal places which are generally considered in analysis. If for most *inorganic* compounds no difference of importance is effected, in the case of the analysis of *organic* compounds it is otherwise.

In this field no one would be expected to reckon with $H = 1.0025$. After H has once been decided upon as $= 1$, it makes quite a difference in the result whether O is taken as 15.96 and C as 11.97, or O as 16 and C as 12. In some cases this difference is greater than the difference in the composition of closely related compounds.

The table given below shows the percentages of hydrogen and carbon in the paraffins containing 30 and 31 carbon atoms and

their derived alcohols and acids (myricyl alcohol and melissic acid[1]), and also the amount of water and carbon dioxide produced in their combustion. Under *a* are the results calculated with $O = 15.96$, $C = 11.97$, under *b* with $O = 16$ and $C = 12$.

	H_2O		H		CO_2		C	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
$C_{30}H_{62}$	132.22	132.23	14.723	14.692	312.68	312.80	85.277	85.308
$C_{31}H_{64}$	132.10	132.11	14.710	14.679	312.73	312.84	85.290	85.321
$C_{30}H_{62}O$	127.39	127.40	14.186	14.155	301.26	301.37	82.163	82.192
$C_{31}H_{64}O$	127.42	127.43	14.190	14.159	301.66	301.77	82.272	82.301
$C_{30}H_{60}O_2$	119.46	119.47	13.303	13.274	291.94	292.04	79.620	79.646
$C_{31}H_{62}O_2$	119.74	119.74	13.334	13.305	292.61	292.70	79.802	79.828

Thus we see that the amount of water remains almost the same in each calculation because the variations compensate each other; the hydrogen on the other hand varies a few hundredths, as does also the carbon, while the variations in the carbon dioxide reach the tenths of a per cent., *a difference which is often greater than that obtained from two adjacent hydrocarbons in a homologous series.* This last is more clearly seen if we calculate by both methods the percentages of carbon and dioxide contained in a series of hydrocarbons, and place them together as is done in the following table.

	$C_{24}H_{50}$	$C_{25}H_{52}$	$C_{26}H_{54}$	$C_{27}H_{56}$	$C_{28}H_{58}$	$C_{29}H_{60}$	$C_{30}H_{62}$
C $\{$ *a*	85.176	85.196	85.214	85.232	85.248	85.263	85.277
$\{$ *b*	85.207	85.227	85.246	85.263	85.279	85.294	85.308
CO_2 $\{$ *a*	312.310	312.384	312.452	312.516	312.575	312.630	312.681
$\{$ *b*	314.426	312.500	312.568	312.632	312.690	312.745	312.796

This shows that the different calculations *a* and *b* may lead to different interpretations of the analyses. If, for instance, the combustion of a hydrocarbon yields 312.51 mg. of carbon dioxide for every 100 mg. of substance, the advocate of Prout's hypothesis will find that the formula $C_{25}H_{52}$ best expresses the result of the analysis, while according to Stas and his followers it indicates the formula $C_{27}H_{56}$. Of course, no one would determine the formula of such a body by means of analysis alone; still, one is accustomed in the choice of formulas to lay a certain weight on the mean result of a series of closely agreeing analyses, and this would here lead to a false conclusion if an error of a few thousandths

[1] Cf. F. Schwalb, Ueber die nicht sauren Bestandtheile des Bienenwachses. Inaug. Diss. Tübingen, 1884.

in the atomic weight of hydrogen were not thought worthy of account.

Those who think with us that the determinations thus far submitted render more probable the relation

$$O : H = 15.96 : 1 = 1 : 0.06265,$$

than that demanded by Prout's hypothesis,

$$O : H = 16 : 1 = 1 : 0.06250,$$

are guilty of a dangerous inconsistency when they operate with such atomic weights as

$$O = 16, C = 12, Cl = 35.46 \text{ or even } 35.5, \text{ etc.}$$

These may, of course, be used in the laboratory for the calculation of approximate results, as in the case of preparing substances; but when it comes to calculating accurate analyses they should not be used.

We may ask of the admirers of Prout's hypothesis whether the universal acceptance of a uniform basis for all atomic weight determinations is not of much more value than a supposition which, in a few cases, may possibly not be entirely erroneous?

We are all convinced that the relation under consideration (and thereby every other atomic weight referred to $H = 1$) is not accurate to the thousandth part of its value. Let us accept it without artificial interpretations, just as it is yielded as the mean value of agreeing results obtained in many different ways, and wait till the future for its further proof and confirmation by experimental methods. As soon as this is accomplished we will be ready, among the first, to accept any changes in the values of the atomic weights as now calculated that may then be deemed necessary.

THE ATOMIC WEIGHT OF SILVER AND PROUT'S HYPOTHESIS.[1]

BY LOTHAR MEYER AND K. SEUBERT.

The calculation of the atomic weights of many of the elements depends, as is well known, upon that of silver, so that the sharpest possible determination of this is desirable in order to obtain

[1] See Berichte der deutschen chemischen Gesellschaft **18**, 1098. Translated by W. S. Bayley.

accurate results, without which a discussion of Prout's hypothesis, *as far as this is concerned with facts*, is unprofitable.

For this reason J. S. Stas, in his masterly investigations, used the utmost care in fixing the stoichiometrical relations between silver and oxygen, and confirmed these by indirect methods with wonderful accuracy. The hypothesis of Prout, that all atomic weights are rational multiples of that of hydrogen, is not borne out by Stas' work; even when the relation of oxygen to hydrogen $=$ 15.96 : 1 is rejected as doubtful and 16 : 1 is taken in its stead, silver and a number of other elements, among them those whose ratio to hydrogen is most accurately known, differ in their atomic weights far more from whole numbers than experimental errors can account for. The accuracy and reliability of Stas' results seemed so far beyond all doubt that one of the most celebrated advocates of Prout's hypothesis could explain the contradiction of the theory by the experiments only by questioning the stability of the foundation of the atomic theory, *the constancy of chemical proportions*, and consequently the possibility of preparing chemically pure substances.[1]

In 1878 Dumas,[2] also a supporter of Prout's teaching, published the results of a few experiments, in which he succeeded in separating oxygen from pure silver which had been fused with a mixture of borax and saltpeter. A kilogram of the silver was heated to redness in a flask connected with a Sprengel's pump, and the evolved oxygen collected and measured.

For each kilogram of silver there were obtained in four different experiments 82, 226, 140 and 249 milligrams of oxygen.

As Stas subjected the silver used in his investigations to the same treatment, this too, as Dumas claimed, must have contained oxygen. In spite of all the care and skill of the experimenter, his results with metallic silver were affected by a constant error which increased the atomic weight of the silver and lowered those of the halogens; the relation of silver to chlorine instead of being 108 : 35.47 as was then generally believed, became 108 : 35.5, in accordance with Prout's hypothesis.[3]

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[1] Marignac, Archives des sciences physiques et naturelles (nouv. pér.) **9**, 1860, p. 105 and ff. "Il ne m'est pas absolument démonstré, que bien des corps composés ne renferment pas constamment et normalement un excès, très faible sans doute, mais sensible dans des expériences très-délicates, de l'un de leurs éléments." See also Ann. Chem., Suppl. IV, p. 202.

[2] Compt. rend. **86**, 65–71. Ann. chim. phys. [5], **14**, 289.

[3] A conclusion of Dumas' which can be contested on more grounds than one. See below.

It cannot be denied that this objection is worthy of attention, and we are justified consequently in briefly considering its effect on the result by briefly discussing a few experiments.

If Stas really worked with silver containing oxygen his error will consist in this, that instead of using 1000 parts of silver he used only 999.751 parts.[1] In transforming silver into silver chloride, Stas obtained by four different methods,[2]

> from 969.3548 grams Ag 1287.7420 grams AgCl,
> in which Ag : AgCl = 1 : 1.32845.

This relation is changed by Dumas' correction into

> 969.1134 grams Ag = 1287.7420 grams AgCl,
> or Ag : AgCl = 1 : 1.32872.

In the same way the correction may be applied to the cases in which silver was changed into silver bromide or iodide by synthesis. In all these cases the error might possibly have reached the maximum as observed by Dumas.

Fortunately, however, a number of experiments were made from which the amount of oxygen contained in the silver can be determined. These consist of *complete syntheses of silver bromide and silver iodide*, when the amounts of both constituents used as well as the resulting compound were weighed.

In both cases the weight of the product was found to be somewhat too low, a result which can be referred to the oxygen in the silver.[3]

The complete synthesis of the silver bromide yielded these figures:[4]

$$Ag : Br : AgBr = 210.5711 : 156.0098 : 366.5639 \text{ grams} \quad [4]$$
$$Ag + Br = 366.5809$$
$$AgBr = 366.5639$$
$$\overline{}$$

Difference, .0170

Calculated for the amount of silver used, this difference corresponds to 0.08073 pts. of oxygen in 1000 pts. of silver, provided the

[1] In the most unfavorable case, when the silver contains the largest amount of oxygen observed by Dumas, viz. 0.249 pts. per 1000.

[2] Lothar Meyer and Karl Seubert, Die Atomgewichte der Elemente. Leipzig, 1883, p. 55 and 56, No. 41 g.

[3] As the difference in the case of the synthesis of silver bromide was smaller the more carefully the bromine was dried, this must in part be due to moisture in the bromine. Besides there was a small loss occasioned by washing.

[4] Die Atomgewichte der Elemente, etc., p. 57, No. 42, b. β.

total loss were due to escape of oxygen. The corrected weight of the silver then becomes 210.5541 grams.

$$\text{Then } Ag : AgBr = 210.5541 : 366.5639$$
$$= 1 : 1.74095$$
$$\text{instead of } 1 : 1.74081$$

Similarly, in the complete synthesis of silver iodide the weight of the product is less than the sum of the weights of iodine and silver.

Stas found[1]

$$Ag : I : AgI = 324.2571 : 381.1262 : 705.3718 \text{ grams} \qquad [5]$$
$$Ag + I = 705.3833$$
$$AgI = 705.3718$$

$$\text{Difference, } \quad .0115$$

This difference corresponds to .03547 parts of oxygen in 1000 of silver, so that the weight of pure silver used was 324.2456 grams. Consequently,

$$Ag : AgI = 324.2456 : 705.3718$$
$$= 1 : 2.17542$$
$$\text{instead of } = 1 : 2.17535$$

The comparison of these values with those obtained from the analyses of the chlorates, bromates and iodates gives the relation of silver to oxygen.

Stas found

$$AgClO_3 : AgCl = 398.3177 : 298.4250 \text{ grams}[2] \qquad [2]$$
$$AgBrO_3 : AgBr = 188.5332 : 150.1671 \text{ grams}[3] \qquad [2]$$
$$AgIO_3 : AgI \quad = 331.6101 : 275.3235 \text{ grams}[4] \qquad [3]$$
$$\text{Or,} \quad AgCl : O = 8.9614 : 1$$
$$AgBr : O = 11.7420 : 1$$
$$AgI : O \quad = 14.6742 : 1$$

Evidently these figures cannot be influenced by Dumas' correction, as there was no metallic silver weighed. From these figures the relation of the silver to the oxygen can easily be calculated by means of the formula[5]

$$\frac{Ag}{AgR} \cdot \frac{AgR}{O} = \frac{Ag}{O},$$

[1] Die Atomgewichte der Elemente, etc., p. 59, No. 43 b. γ.   [2] *Ibid.* p. 47, No. 35 b.
[3] *Ibid.* p. 47, No. 36.   [4] *Ibid.* p. 48, No. 37 b.   [5] *Ibid.* pp. 50-52.

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in which R is one of the halogens Cl, Br or I.   According to this,

$$Ag : O = \frac{8.9614}{1.32872} = 6.7439 : 1$$

$$Ag : O = \frac{11.742}{1.74095} = 6.7446 : 1$$

$$Ag : O = \frac{14.6742}{2.17542} = 6.7455 : 1$$

Of these three numbers, neither of which agrees with the 6.7500 demanded by Prout's hypothesis, the third is entitled to most consideration; for, in the first an arbitrary correction is made, in the second a part of the error credited to oxygen must surely be due to some other impurity, the third is calculated from experiments made with the purest materials.   This number 6.7455, obtained from the complete synthesis of silver iodide and the analysis of the iodate, is also the mean of several other determinations made by Stas which vary between 6.7451 and 6.7458; besides, it is almost identical with 6.7456 yielded by silver iodide and iodate without the application of Dumas' correction, as well as the 6.7456 obtained by reducing silver sulphide and sulphate.

The conclusion is consequently justified, since several of Stas' determinations agree satisfactorily with one another and with the number which is certainly free from the error pointed out by Dumas, that the influence of this is confined within the limits of error and consequently may be neglected.

If it appears strange that the silver used by Stas for determining the atomic weight exhibited only in small degree an impurity, whose amount was determined by the experiments of Dumas as being quite considerable, it must be remembered that only the oxygen present in a condensed form would influence the weight; the gaseous oxygen under the normal pressure producing an effect scarcely more noticeable than the air in which the silver was weighed.   Besides, Stas always heated his silver to dark redness immediately before weighing, so that the greater part of the "occluded" oxygen either escaped or was changed into the gaseous form.

These considerations, based on the results of experiments, show, as we again emphasize, *that the determinations of the atomic weight of silver by Stas are not appreciably influenced by the oxygen which the silver retains within itself.*[1]

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[1] W. Ostwald reached the same conclusion through the theory of probabilities. See his Lehrbuch der allgemeinen Chemie, 1884, **1**, 35.

The atomic weight of silver then is, if $H = 1$ and $O = 15.96$,
$$Ag = 107.66$$
$$\text{if } O = 16, \; Ag = 107.93;$$
while the figures calculated from the results of the experiments with metallic silver and silver chloride are, after applying the correction of Dumas,

$$Ag = 107.63, \text{ if } O = 15.96, \text{ and}$$
$$Ag = 107.90, \text{ if } O = 16.00.$$

Thus we see that the atomic weight of silver is removed still farther from the whole number required by Prout's hypothesis, by the application of Dumas' correction; chlorine also still remains inconsistent with it, while a few other elements, like potassium, sodium, etc., approach or depart from it according as we take $O = 16$ or 15.96. Dumas has assumed, in order to explain such exceptions to Prout's hypothesis as chlorine particularly offers, that hydrogen itself is composed of ultimate atoms (uratomen), of which he at first thinks there are two in one atom of hydrogen, but when this is also found not to be in accordance with the experimental results, increases the number to four.

But even this "elastic modification," as Clarke calls it, of the old theory can only be preserved, in the face of Stas' work, by decreasing the size of the unit, that is the weight of the ultimate atom, in proportion as the accuracy of our experimental work increases.

More recently,[1] the universal ether, with an atomic weight of 0.0001 $(H = 1)$, has been assumed as the primitive substance of which all other elements were formed. The atomic weights of all other elements must of course be whole multiples of this, since none of them have been accurately determined to the fourth decimal place, while many are certain only to the first or second place, and some only to units of hydrogen.

Nor need it excite wonder if, as has been proposed by another writer,[2] every atomic weight y can be approximately calculated by the expression:
$$y = p \; 15 - 15 \, (0.9375)^x \text{ or,}$$
$$y = 15\left(p - \left(\frac{15}{16}\right)^x\right),$$

---

[1] M. Zängerle, Über die Natur der Elemente, etc. Programm des Kgl. Realgym. München, 1882.

[2] Edm. J. Mills, On the Numerics of the Elements, Philos. Mag., Nov. 1884, p. 393.

in which p may vary between 1 and 16, but x varies from 1–50, or even ∞ ; for the fraction $\dfrac{15}{16}$ so nearly approaches unity that any number can be accurately expressed by the formula.

Speculations of this kind are far removed from any possibility of experimental proof, and can therefore never be expected to receive from it any support. Nor can we ever hope to receive any essential extension of our knowledge in respect to primitive matter (urmaterie) through a more accurate establishment of the atomic weights; the next important progress will rather be brought about by the decomposition of the elements into a similar substance, differing from them however, which may be the primitive matter itself, or a condensation product of it. The solution of this question, that is, the decomposition of all the elements into one and the same original substance, we can hardly ever expect to accomplish.

From the atomic weight of silver, determined, as above shown, with the greatest accuracy, and from those of the other important elements[1] calculated by its means, it follows as a consequence that *the atomic weight of silver, as well as the atomic weights of numerous other elements, all contradict Prout's hypothesis in its characteristic original conception; it must therefore be looked upon as having been disproved by experiment.* In its new forms it has likewise been disproved, so far as this is possible in the present state of our knowledge. Beyond this it amounts merely to philosophical speculation concerning an idea whose probable correctness will be denied by no one,[2]—the unity of matter.

EYSTER'S SCHEME FOR QUALITATIVE ANALYSIS.

By Robt. B. Warder.

In the last number of this Journal (pp. 21–26) appears a method for the qualitative determination of the bases without direct use of hydrogen sulphide, which will prove very convenient in many

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[1] Cf. Atomic weight tables of Meyer and Seubert. Breitkopf u. Härtel, Leipzig, 1884.

[2] Cf. Lothar Meyer, Moderne Theorien, V. Auf. p. 134.

cases. Having used this method in part with my own classes during the past year, a few notes may be of service to those who have not yet tried it.

The use of sulphuric acid to precipitate Ba, Sr, Ca and Pb (as copied from Zettnow's scheme) appears to be a needless complication and may be simply omitted, other provision being made for the detection of these metals.

The principle underlying Eyster's most important modification will be seen at a glance from the following table ; from which also an outline of the scheme may be deduced.

Basis of Usual Scheme.

Basis of Eyster's Scheme.

Sulphides precipitated by H₂S in presence of HCl.

$$
\begin{cases}
\text{Sol. in} \\
\text{Am}_2\text{S}
\end{cases}
\begin{cases}
\text{As} \\
\text{Sb} \\
\text{Sn}
\end{cases}
\qquad
\left.\begin{array}{}\end{array}\right\}
\begin{array}{l}\text{Sulphides sol.}\\ \text{in Am}_2\text{S.}\end{array}
$$

Insol. in Am₂S — Hg, Pb, Bi, Cd, Cu — Insol. in cold dilute HCl

Ni, Co, Zn, Mn, Fe, Al, Cr

Not precipitated by H₂S in presence of HCl.

Zn, Mn, Fe, Al, Cr — Sol. in cold dilute HCl

Sulphides (or hydrates) precipitated by AmOH and Am₂S.

Cobalt and nickel hold an exceptional position, their sulphides being practically insoluble in cold dilute chlorhydric acid, and yet not precipitated in presence of that reagent by hydrogen sulphide. Under the new scheme they are dissolved by nitric acid, and held in solution by excess of ammonia with the cadmium and copper. Eyster precipitates the four sulphides (after testing for Cu with ferrocyanide), dissolves the cadmium with sulphuric acid, and tests for nickel with the bead in presence of copper. My own experiments show that cadmium may also be separated from nickel and cobalt by adding ammonium sulphide in presence of potassium cyanide, and the following provisional scheme is offered :

Add KCy and Am₂S, yellow precipitate, *cadmium.*
Add C₂H₄O₂ to filtrate, black precipitate, *copper.*
Add HCl to filtrate, black precipitate, *nickel.*
Look for Co in solution.

This use of acetic and chlorhydric acids was proposed by Mr. J. Swearingen, and has been partially tested in this laboratory by himself and by Mr. E. G. Eberhardt. Acetic acid precipitates copper at once ; a part of the cobalt also separates on standing one or two days.

In a mixture of cobalt and nickel sulphides, the former (as is well known) can usually be detected at once with the borax bead. The latter may be partly dissolved in yellow ammonium sulphide and reprecipitated by chlorhydric acid. I have rarely failed to obtain a sufficient quantity of nickel by this means to give distinct color to the bead.

Details will be found in Eyster's careful paper, which has induced me to present these notes at once, instead of waiting to make a more thorough examination of the special features proposed.

PURDIN UNIVERSITY, LAFAYETTE, IND., *May* 9, 1885.

ESTIMATION OF ARSENIC IN ORES, MATTES AND METALLIC COPPER.

By G. W. LEHMANN AND W. MAGER.

In the course of professional work at our laboratory it has become necessary to determine small quantities of arsenic, and after testing the methods proposed for this purpose, we have found that proposed by R. Pearce[1] to be the most reliable and convenient. This consists in mixing the finely powdered substance with about six times its weight of equal parts of sodium carbonate and potassium nitrate, fusing and extracting with hot water, and filtering. The filtrate is then acidified with nitric acid, and boiled to expel carbonic and nitrous acids. To the cool solution silver nitrate is added, and then ammonia to neutral reaction. The silver arsenate is filtered, washed out with cold water until no silver is found in the washings, and the silver determined by Volhard's method. 108 parts of silver correspond to 25 parts of arsenic. Numerous experiments

[1] See Engineering and Mining Journal, May 5th, 1883, p. 256.

with ores and mattes (free of arsenic) mixed with known quantities of chemically pure arsenious oxide, and containing lead, antimony and aluminium salts (purposely added), convinced us of the accuracy of the method. Now the question arose how this method could be best applied to metallic copper containing about one-tenth per cent. of arsenic.

We found it most convenient to precipitate the arsenic in combination with oxide of iron. Considering that metallic copper very rarely is free from arsenic, and that borings taken from different parts of the same ingot contain different quantities of arsenic, we dissolved in each case 100 grams of copper in nitric acid, diluted to 500 cc. with water, and took 100 cc. (20 grams) for each determination.

In the first 100 cc. we determined the arsenic contained in the copper; to the second and third 100 cc. we added known quantities of arsenic which had been prepared by fusing chemically pure arsenious oxide with sodium carbonate and potassium nitrate and dissolved in nitric acid, and deducted the first result from the last. We proceeded in the following way : A piece of iron sulphate, about the size of a pea, was dissolved in nitric acid, added to the copper solution, and then ammonia in excess ; the solution was well stirred and the precipitate of oxide of iron filtered hot, washed out with hot water, dried, removed carefully from the filter, mixed with the fusing mixture, etc. In another series of experiments we added lead and antimony, and found that their presence did not interfere with the results. (A solution containing both metals in considerable quantity gave 0.131 per cent. and .144 per cent. arsenic, when 0.134 per cent. arsenic was present.)

The following results show the accuracy of the method :

As present.	As found.	
0.0701 per cent.	0.0615 per cent.	0.0596 per cent.
2.87 "	2.82 "	2.94 "

0.0118 gram As_2O_3 (used in these experiments) gave .00907 gram As. Calculated .00894 gram As.

As present.	As found.	
0.1 per cent.	0.1004 per cent.	As $Mg(NH_4)AsO_4 = .092$ per cent.
	0.0953 "	

MINOR INVESTIGATIONS.

By L. M. Norton.

I. *Oxidation of Benzol.*

The action of a powerful oxidising agent upon benzol has been occasionally investigated, but the unexpected results obtained in certain cases have hardly attracted the attention they deserve. The formation of benzoic acid by the oxidation of benzol is certainly worthy of notice.   Under my direction Mr. J. G. Holder has repeated some previous experiments in this direction, and we have also attempted the oxidation of benzol by some methods not heretofore employed. I give a summary of our experiments. The benzol used in all the experiments boiled between 80.2° and 80.3°, and left no residue at the latter temperature.   Our analysis gave figures which corresponded to 92.20 per cent. of carbon and 7.70 per cent. of hydrogen, while the theory requires 92.30 per cent. of carbon and 7.70 per cent. of hydrogen.   Its perfect freedom from toluol is certain, as long continued boiling with dilute nitric acid and also with a solution of chromic acid in acetic acid failed to furnish the least trace of benzoic acid.   Carius[1] first investigated the action of binoxide of manganese and sulphuric acid upon benzol and obtained carbonic anhydride, formic acid, benzoic acid and a phthalic acid.   We investigated this method of oxidation under somewhat different conditions with a somewhat different result.   Three large flasks were taken and 100 grams of benzol placed in each.   The benzol was carefully cooled, and a mixture of 600 grams of ordinary pure sulphuric acid and 120 grams of water slowly added to each flask, all heating being carefully avoided.   Next, 100 grams of powdered MnO_2 were stirred into the mixture in each flask and the mixture then allowed to stand one week, with frequent stirring.   The undecomposed benzol was then removed by distillation, the acid nearly neutralised with caustic soda and evaporated to a small volume, and this liquid treated with ether, which removed an organic acid from the liquid.   This acid was then purified.   It sublimed without decomposition, agreed

[1] Ann. d. Chem. **148**, 50.

in all physical properties with benzoic acid, and furnished barium
and calcium salts, which, upon analysis, proved to be the benzoates
of barium and calcium. The yield of benzoic acid is small. Car-
bonic anhydride was the other product of the oxidation which we
observed. We were unable to convince ourselves of the presence
of formic or phthalic acids.

We next examined the action of peroxide of lead and sulphuric
acid upon benzol. By the action of these agents upon benzoic
acid Meissner and Shepard[1] obtained succinic acid and carbonic
anhydride. Benzol and PbO_2 were shaken together in a flask and
sulphuric acid (sp. gr. 1.56) run in from a drop-funnel. Vigorous
action accompanied by frothing takes place in the cold at first,
afterwards gentle heating is required to complete the action.
After 12 hours heating the undecomposed benzol was removed
by distillation, the liquid diluted with water and filtered. The
black residue consisted mostly of PbO_2 and $PbSO_4$ and contained
no organic acid. The clear liquid was treated with $BaCO_3$ in
excess, filtered and the filtrate evaporated to dryness. It furnished
a barium salt soluble in water, containing 36.50 per cent. of barium
and corresponding in every respect with benzoate of barium. The
free acid from this salt showed all the physical properties of
benzoic acid. The yield is much larger than by the action of
MnO_2 and H_2SO_4 upon benzol. Carbonic anhydride is formed
also in large quantities in the oxidation with PbO_2 and H_2SO_4.

The statements regarding the action of potassium permanganate
upon benzol differ. Berthelot[2] obtained oxalic acid by the action
of alkaline permanganate solution upon benzol, while Adrienz[3]
found formic acid to be the product of the oxidation in an acid
solution. The action is certainly very slow. A neutral solution
of permanganate failed to attack benzol perceptibly in two weeks,
as was proved by the weight of benzol recovered. A strongly
acid solution in 12 days oxidised one-fourth of the benzol present,
but we could not detect the production of solid or liquid products,
while boiling with alkaline permanganate solution for six hours
failed to oxidise any of the benzol.

We examined the action of PbO_2 and dilute nitric acid upon
benzol. We boiled 50 grams of benzol, 104 grams of nitric acid
(sp. gr.1.4), 222 grams of water and 30 grams of lead peroxide

[1] Zeit. f. Chem. 1866, 752.   [2] Compt. rend. **64**, 35.

[3] Berichte der deut. chem. Gesell. **6**, 443.

with a return cooler for 60 hours. After removal of the undecomposed benzol, the dilute acid deposited a crop of crystals which proved to consist of oxalic acid and no other oxidation product was observed. Leeds[1] obtained oxalic acid by the oxidation of benzol with ozone and with hydrogen peroxide.

By oxidising benzol with a solution of chromic acid in acetic acid and also by the action of potassium bichromate and sulphuric acid we obtained only carbonic anhydride.

II. *Action of Isobutyric Acid upon Aniline.*

Under my direction, Mr. F. L. Bardwell has examined the action of isobutyric acid upon aniline in the presence of zinc chloride. Kahlbaum's isobutyric acid was mixed with pure aniline in the proportion of one molecule of the acid to one molecule of aniline. The liquids were shaken together, but no evidence of chemical action could be detected; a small quantity of anhydrous zinc chloride was then added, whereupon the mixture at once turned to a mass of crystals, and a decided rise in the temperature of the mixture was observed. The crystals were easily soluble in water, and were decomposed by dilute caustic alkalis in the cold and aniline set free. The crystals were doubtless aniline isobutyrate. The crystalline mass obtained by the action described above was placed in a flask, melted, and boiled for from one to two hours beneath a return cooler. At the end of this time the flask was cooled, and contained then a solid mass of crystals. These crystals were washed with dilute hydrochloric acid to remove any undecomposed aniline. They proved to be somewhat soluble in cold water and easily soluble in hot water. Caustic alkalis did not attack them in the cold, but upon heating, decomposed them, furnishing aniline. The substance was crystallised repeatedly from water, and analysed when the melting point was constant, with the following results:

0.1535 gram of substance furnished 0.1130 gram of H_2O and 0.4165 gram of CO_2.

0.9110 gram furnished 68.14 cc. of N at 20° and 760 mm.

	Found.	Theory for isobutyranilide.
H	8.54 per cent.	7.97 per cent.
C	73.99	73.61
N	8.56	8.58

[1] Berichte der deut. chem. Gesell. **14**, 975.

These results show conclusively that the substance is isobutyr-anilide, isomeric with the butyranilide obtained by Gerhardt,[1] by the action of a mixture of butyric acid and butyryl chloride upon aniline. Isobutyranilide crystallises from water in colorless prisms which melt at 102.5° without decomposition. It distills also with-out decomposition. It is somewhat soluble in cold water, easily soluble in hot water, alcohol and ether. The yield of the anilide is increased by heating the mixture of aniline, isobutyric acid and zinc chloride in closed tubes at 150°. If aniline and anhydrous isobutyric acid are heated without zinc chloride in a similar manner, the anilide can be obtained, but only with difficulty and in small quantities.

Nitric acid acts with great violence upon isobutyranilide, and all attempts to isolate a nitro compound in a pure condition failed. By the action of bromine upon the anilide a monosubstitution product was obtained. The anilide was dissolved in cold water, and a current of air charged with bromine vapor passed through the solution. A heavy precipitate of a yellowish color separated. This substance was very insoluble in water, but readily soluble in hot dilute alcohol. It was purified by repeated treatment with animal charcoal in an alcohol solution, and repeated crystallisations from this solvent, and was finally obtained in colorless needle-shaped crystals.

A bromine estimation furnished the following figures: 0.1569 gram furnished 0.1220 gram of AgBr.

	Found.	Theory for $C_6H_4BrNHC_4H_7O.$
Br	33.15	33.05

The bromisobutyranilide melts at 128°, but can be sublimed undecomposed at a somewhat lower temperature. It is soluble in hot water and slightly in cold water, but could not be obtained from water in a crystalline form. It is easily soluble in alcohol. It is unaffected by cold caustic alkali, but hot caustic alkali dis-solves it slowly without decomposition. By heating in a closed tube at 125° for several hours, with aqueous hydrochloric acid, it was decomposed and furnished the hydrochloride of parabrom-aniline. The free base obtained from this hydrochloric acid salt melted at 67°.[2] The compound obtained by the action of bromine upon isobutyranilide is therefore parabromisobutyranilide. The formation of an isomer was not observed. The parabromiso-

[1] Ann. d. Chem. 87, 166.   [2] Körner, Jahres. f. Chem. 1875, 356.

butyranilide was treated with a mixture of nitric acid and sulphuric acid, in the manner recommended by Nölting and Collin[1] for the production of nitracetanilide, and furnished a nitro compound difficult to purify, but which after repeated crystallisations from alcohol yielded a yellow crystalline product, melting at 111.5°, containing 36.37 per cent. of bromine, and agreeing in all respects with para-bromorthonitraniline.[2]

III. *The Ethylorthotoluidines.*

In the course of an investigation upon the products of oxidation of the substituted aromatic amines, Mr. R. L. Chase has prepared under my direction the ethylorthotoluidines. These compounds were prepared by Reinhardt and Staedel,[3] but they furnished no description of their characteristics.

Ethylorthotoluidine.

Ethyl iodide combines with great readiness with orthotoluidine. If mixed in the proportion of 1 mol. of ethyl iodide to 1 mol. of orthotoluidine, and allowed to stand for twelve hours at the ordinary temperature, the mixture becomes a solid crystalline mass consisting of the hydriodide of ethylorthotoluidine. We dissolved this salt in water, in which it is very soluble, and added caustic potash solution, by which a base was set free as an oil. This oil dried over $CaCl_2$ and fractionated, furnished a product which boiled at 204°–206°, and gave the following figures upon analysis:

	Found.	Theory for ethylorthotoluidine.
C	79.52	80.00
H	10.03	9.63
N	10.34	10.37

Ethylorthotoluidine is a thin yellowish oil which gradually turns pink upon standing. Our product boiled at 204°–206°, and remained liquid at —15°. Its specific gravity is .9534 at 15.5° compared with water at the same temperature. Its platinum salt separates as an oil, and cannot be obtained in a state of purity owing to the ease with which it is decomposed. It resembles

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[1] Ber chte d. deut. chem. Gesell. **17**, 262.

[2] Hübner, Retschy, Berichte d. deut. chem. Gesell. **6**, 796, and Körner, Jahres. f. Chem. 1875, 328.

[3] Berichte d. deut. chem. Gesell. **16**, 29.

closely the corresponding salt of ethyl paratoluidine.[1] The hydrochloric acid salt of the base could not be isolated. The hydriodic acid salt separates from water as a jelly, but can be crystallised from alcohol, in which it is less soluble. An iodine estimation in the hydriodide thus purified gave 48.39 per cent. of iodine, while the theory requires 48.29 per cent. The acet-compound can be obtained either by the action of acetyl chloride or acetic anhydride upon the base. It is somewhat soluble in water, easily soluble in alcohol and benzol, and separates from these solvents as an oil. It boils between 254°–264°, and solidifies after long standing.

A nitrogen estimation in the acet-compound gave,

	Found.	Theory for acetethylorthotoluidine.
N	8.34 per cent.	7.91 per cent.

The ethylorthotoluidine furnishes by the method employed by Fischer[2] for preparing nitrosomethylaniline, a nitroso compound. This compound was purified by distillation with steam, and is a dark brown oil which cannot be distilled alone without decomposition. A nitrogen estimation gave,

	Found.	Theory for nitrosoethylorthotoluidine.
N	16.63	17.05

Diethylorthotoluidine.

When ethylorthotoluidine is heated with an excess of ethyl iodide at 100° for six hours in a closed tube the mixture turns to a mass of white crystals soluble in water. An aqueous solution of this salt treated with caustic potash solution yielded a free base, which was dried over $CaCl_2$, fractionated, and proved upon analysis to be diethylorthotoluidine.

	Found.	Theory for diethylorthotoluidine.
C	80.54	80.98
H	11.06	10.43
N	9.25–9.23	8.58

Diethylorthotoluidine appears to have been first prepared by Baeyer and Caro,[3] but is not described by them. Our product boiled between 203°–208°, and was a limpid oil, closely resembling the mono-compound. Its hydriodide is less soluble in water

than that of ethylorthotoluidine, and crystallises from it in beautiful prisms, which contain 1 mol. of water of crystallisation, and melt at $72°–73°$. An iodine estimation in the anhydrous salt gave 43.78 per cent. of iodine, while the theory requires 43.64 per cent. The yield of diethylorthotoluidine was 70 per cent. of the theoretical quantity.

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THE OPTICAL PROPERTIES OF MALIC AND TARTARIC ACIDS.

BY LOUIS BELL.

Among optically active substances, these two acids have long been recognised as showing remarkable and inexplicable peculiarities. Much alike in chemical character, their optical properties are in most respects identical. Both show an increase of optical activity with a rise in temperature or with a decrease of concentration ; both, in strong solution or at a low temperature, show a tendency to reverse the normal direction of optical rotation, and finally, under proper conditions, both actually reverse this direction, laevo-malic acid becoming dextro-rotatory, and dextro-tartaric acid becoming laevo-rotatory. Furthermore, each exists in a form itself optically inactive, but which may be split up into two forms, crystallographically enantiomorphous, and possessing optical activities sensibly equal and opposite.

This fact was shown for tartaric acid by the classical research of Pasteur,[1] while Bremer[2] extended it to malic acid. The optical properties correspond to the crystalline form so distinctly as to make it evident that the molecular structure which produces optical activity also induces crystalline asymmetry.

Both these acids also exhibit variable and anomalous rotary dispersion ; tartaric acid in a very marked degree. In all respects their optical behavior is so nearly identical that facts established by investigation of the one will uniformly be true of the other.

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[1] Ann. de Ch. et de Phys. (2) **24**, 442.   [2] Ber. d. deut. chem. Ges. **13**, 351.

To explain some of these peculiarities, and, in particular, to assign a cause for the reversal of the direction of rotation, a phenomenon which implies some profound physical change, the following inquiries have been instituted.

The property of twisting the plane of polarisation is almost certainly due to some condition of asymmetry, either molar or molecular. In crystals it is always associated with enantiomorphs, in liquids it must be due to asymmetrical grouping or asymmetrical configuration of the molecule itself, while in gases it is quite certain that only the latter cause can operate.

In any case a change in the direction of this twisting is a change not of degree but of kind, and must involve an altered configuration of the material system upon which the ether waves impinge. In case of liquids, Le Bel[1] has shown optical activity to be associated quite constantly with the presence of an asymmetrical carbon atom.

In the consideration of malic and tartaric acids the increase of specific rotation on dilution calls for careful attention. It was first investigated by Biot in case of tartaric acid, but all that he could offer by way of explanation[2] was the extraordinary hypothesis that the acid impressed its optical properties on the whole mass of water with which it was mingled. In a problem essentially dynamical, this sort of explanation can have but little weight, and the solution must be sought elsewhere. It is evidently connected with the reversed rotation into which it gradually passes, and this in turn must plainly be associated with some change either in the molecules themselves or in their form of aggregation. Given a number of molecules twisting the plane of polarisation in a given direction, and there are four classes of causes which could reverse that direction. 1. Change of configuration of the molecule itself; 2. Formation of a hydrate or other chemical compound; 3. Building up of crystalline forms; 4. Formation of a polymeride rotary in the opposite sense from the free molecules. It is well to discuss these possibilities in order.

1. It does not seem probable that such a change could be produced by simple dilution, unaccompanied as it is by any marked thermal effects. Further, we know that the change can be produced, as when racemic acid is prepared from dextro-tartaric, but it is by no means readily effected. To form racemic acid in the

[1] Bull. Soc. Chim. **22**, 337.   [2] Ann. de Ch. et de Phys. (3) **10**, 385.

way mentioned requires heating with water in sealed tubes for many hours to a temperature of 175°.[1] If such treatment is required to produce a laevo-rotatory modification of dextro-tartaric acid, it is highly improbable that it could be effected by any ordinary change in temperature or by any possible amount of dilution. And if the changes in temperature which produce such a marked effect on the optical activity do so by a change of configuration, *i. e.* from dextro to laevo forms, tartaric acid should crystallise in right or left handed hemihedral forms according to temperature. But such is not the case.

2. The hypothesis of a hydrate is at least quite plausible, and seems to have been the one tacitly adopted by many investigators. Biot in his later papers seems to have been inclined to accept it. The existence of a hydrate would explain most of the facts observed, and at first sight would appear very probable, but a close examination shows that no hydrate is formed.

In the first place hydrates are uniformly produced with evolution of heat, and in the case of one of the acids in question (racemic acid), the amount of heat given out has been accurately measured by Berthelot.[2] Hence we are justified in concluding that, if the dilution which so increases the specific rotation of tartaric acid is accompanied by the formation of a hydrate, it must also be accompanied by an evolution of heat. On the contrary, diluting a concentrated solution of tartaric acid causes a slight but unmistakable fall of temperature—the uniform sign of chemical decomposition or physical disintegration. This point was demonstrated in the following way: A small gas-washing bottle was fitted with a very sensitive thermometer passed through the rubber stopper which closed the lateral opening at the bottom. Enough distilled water to cover the bulb of the thermometer (usually 20 cc.) was then poured in, and the contraction in the cylinder was then closed by means of a rubber stopper fitted on the end of a glass rod. About 15 cc. of the solution to be tested was then placed in the upper part of the vessel, and the mouth was closed by a rubber stopper slipped over the rod before mentioned. Thus tightly closed the whole apparatus was immersed in water for some hours. Finally, without taking the vessel from the water or disturbing it in any way, the glass rod was slipped upward far enough to remove the stopper

[1] Jungfleisch, Bull. Soc. Chim. (2) **19**, 99.   [2] Comptes Rendus, **78**, 713.

from the contraction and allow the solution to run into the water. Solutions of tartaric and malic acids of from 20 to 40 per cent. were thus tested, and falls of temperature of from 0.1° to 0.2° were observed. The same is true of solutions of various salts, but the fact is none the less conclusive against the formation of hydrates of the above acids.

Again, since a hydrate is a definite chemical compound, after a hydrate was formed we should expect a condition of comparative stability to be reached, but in tartaric acid there appears to be no such definite compound completed.

Finally, the most characteristic of the optical properties of these acids, *i. e.* reversal of the direction of rotation by change in temperature, was discovered by Biot[1] in amorphous solid tartaric acid, in which case, from total absence of water, the possibility of a hydrate is obviously excluded. Biot had foreseen that a solution of tartaric acid would probably become laevo-rotatory if a sufficient degree of concentration could be reached, but had sought for the complete phenomenon in vain, till he found its analogue in the behavior of melted tartaric acid, which on cooling down passes, like the solution as it is concentrated, through decreasing rotations into a laevo-rotatory amorphous solid. I have recently succeeded in obtaining slight laevo-rotation from a concentrated solution in 95 per cent. alcohol at $-15°$.

Biot, throughout a most careful and exhaustive series of papers covering literally hundreds of pages of the Annales de Chimie et de Physique, was misled by the old formula of tartaric acid $(C_8H_5O_{10} + 2H_2O)$ which represented it as containing water. Consequently he makes use of this hypothetical water even to explain the properties of the melted acid. His experiments, however, were very careful and elaborate, and his papers, scattered through the third series of the "Annales," cover most of the facts concerning rotary polarisation.

The hypothesis of a hydrate being thus excluded, the next possibility is the formation of crystal molecules. This hypothesis was suggested by Dubrunfaut, Erdman and Bechamp,[2] to account for birotation in milk sugar. For several reasons, however, it is not applicable to the present case. Whatever may be the nature of the modification which reverses the rotation in malic and tartaric

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[1] Ann. de Ch. et de Ph. (3) **28**, 351.   [2] Jahresber. f. Chem. 1855, 671 ; 1856, 639.

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acids, it certainly has a rotation direction opposed to that of the free acid. But malic acid shows little tendency to crystallise in any form whatever, and the crystals of tartaric acid correspond in optical character to the solution. Hence any structure that could fairly be called a crystal would not probably show any tendency to reverse the rotation. Further, the formation of crystals would necessitate a change in optical character more rapid than that observed, as will be shown later.

From the consideration of these facts it appears that while the observed facts can hardly be accounted for by the formation of true crystal molecules, a quite similar phenomenon—the formation of a polymeric modification—may prove to be a sufficient explanation.

Such a hypothesis, in the first place, explains and agrees with the phenomena observed. Consider the case of a solution of dextro-tartaric acid, or since the changes are here more rapid, of laevo-malic acid. As the concentration increases or the temperature falls, let a dextro-rotatory polymeride be formed. It is evident that the first effect would be to counteract the original rotation, and there must occur precisely what does occur in the acids in question, a lessening of the initial specific rotation by an increase in concentration or a fall in temperature.

Breaking up of this polymeride by dilution or heating would obviously reproduce the same series of phenomena in the reverse order.

Dissociation has been suggested as a possible cause of analogous optical properties by Oudemans,[1] but he refers it to the breaking up of a salt into its constituents, while in this case it seems to be true dissociation of a polymeride into its simpler and more stable form. Such polymerisation is quite comparable with that exhibited by aldehyde, cyanogen and some other substances, though from the ready solubility of the product the phenomenon is in this case by no means obvious. Oudemans also hints at the possibility of some molecular combination, but this is quite different from a polymeride possessing new and opposite optical properties.

Consider the conditions in such a solution. At any given concentration let m be the number of normal molecules and n the number of polymeric molecules, and let r and r' be their respective rotative powers. Then, evidently, the condition for reversal of rotation is

[1] Liebig's Annalen **166,** 73; **182,** 60.

that $nr' > mr$, where r and r' have opposite signs; while where $nr' < mr$ the normal rotation will be only decreased, and for $nr' = mr$ there will be no rotation. These conditions are general for any mixture of optically active substances.

For the case in question, since the molecule of one of the substances is composed of p molecules of the other, the additional condition is imposed that $np + m = A$, the total number of normal molecules before any formation of the polymer. Under these circumstances the condition for no rotation in terms of m will evidently be $m = \dfrac{Ar'}{rp + r'}$.

From this equation it appears that if r' were due to a crystalline form, in which p must be quite large, and were in magnitude fairly comparable to r, the change produced in the rotation would be large compared to the number of crystal molecules formed. Hence, when the change in rotation is gradual and extends over a wide range of temperature, there is reason to suppose that p is rather small.

Further, since the rotation is a function of the wave-length according to the formula $a = \dfrac{B}{\lambda^2} + \dfrac{C}{\lambda^4}$,[1] all optically active substances must produce dispersion varying for each substance with the constants B and C, but varying in direction with the sign of a. Now if substances be mixed which give opposite signs for a, it is evident that a more or less perfect color compensation can be effected, according to the relative magnitudes of the constants. If these were equal, perfect achromatism would follow together with absence of rotation. If they were unequal, various sorts of irregular and anomalous dispersion must result; and when the rotation of the system is completely reversed, the dispersion will have changed its direction. If one of the substances is more affected by temperature than the other, the constants will vary and irregular dispersion must follow. Anomalous rotary dispersion is inexplicable unless the substance showing it be a mixture, for a is a function only of constants and powers of λ, and in rotary dispersion there is no analogue of absorption. Biot[2] has investigated experimentally this rotary dispersion, and found the partial achromatism, irregular dispersion and allied phenomena indicated above.

[1] Boltzmann, Pogg. Ann. Jubelband, S. 128.   [2] Ann. de Ch. et de Phys. (3) **36**, 405.

Now these theoretical considerations are completely fulfilled by the properties of malic and tartaric acids. As a solution of malic acid becomes more and more concentrated the laevo-rotation gradually decreases, approaches the neutral point, and then, up to the limit of saturation, becomes more and more dextro-rotatory. For a temperature of 20° the neutral point is found in a solution containing 35.3 per cent. of the acid. A 70 per cent. solution has a specific rotation $[a]_D = + 3.3°$.[1] The dextro-rotation of malic acid was first noticed by Arendtsen.[2] These phenomena are precisely what would follow the gradual formation of a polymeride; and if it is so formed, increase of temperature should break it up and restore the laevo-rotation. This actually happens;[3] and without knowledge of the fact, and proceeding on purely theoretical grounds, I found that a solution inactive at 20° could be made to pass from dextro- to laevo-rotation and back with the greatest ease. Further, it is to be noticed that the change of rotation produced by a given change in temperature grows rapidly less as the solutions used are more and more dilute, which phenomenon would be a natural consequence if a polymeride were gradually broken up by dilution, but is incomprehensible if the change is due only to rise of temperature.

In case of sodium malate, which in general shows a stronger tendency to laevo-rotation than the free acid, this phenomenon is far less marked; which seems to indicate that, there being a comparatively small amount of the polymeride formed, the change produced by its dissociation is correspondingly small. I have extended the observations given by Thomsen by measuring the change of rotation produced in a 10 per cent. solution of the acid by rising temperature. From 20° to 40° in a 100 mm. tube the change was less than 20′, from which it would appear that, in a very weak solution, the polymeride is almost completely broken up, and the change produced by heating would be little or nothing.

Tartaric acid is under all ordinary conditions dextro-rotatory, but becomes laevo-rotatory for blue rays in sulphuric acid solution,[4] and completely so for solutions in anhydrous ether, acetone, or alcohol at a low temperature (as previously mentioned). Its

[1] Schneider, Liebig's Annalen **207**, 262.　　　　[2] Ann. de Ch. et de Ph. [3] **54**, 403.

[3] Th. Thomsen, Ber. d. deut. chem. Ges. **15**, 441.

[4] Biot, Ann. de Ch. et de Ph. (3) **10**, 385.

specific rotation, like that of malic acid, increases with the temperature.

But the most conclusive evidence that could be wished is furnished by its rotary dispersion. In a 10 per cent. solution the dispersion is normal, but, as the concentration is increased, anomalous dispersion appears, and passes through various phases, until in a 50 per cent. solution the rotation for the blue is less than for the red ; and the gradual reversal of rotation goes on till, in a 90 per cent. solution, the blue is laevo-rotatory, and the dispersion is that normally belonging to a laevo substance. Furthermore, the same series of changes can be produced by changes in temperature, a 50 per cent. solution showing an entirely normal dispersion at 50°.[1] From these facts it is evident enough that tartaric acid undergoes modification into a laevo-rotatory form by concentration or lowering of temperature. It has been shown that this modification cannot be due to change of configuration or to a hydrate, while the only crystalline form of ordinary tartaric acid known has optical properties opposed to those which must be attributed to the above modification. The hypothesis of a polymeric modification explains the observed facts effectively, and renders the change of specific rotation by dilution comprehensible. For it is clear that a polymeride may be dissociated in this way, since Berthelot[2] has shown by a beautiful series of thermo-chemical experiments that racemic acid, which is well known to be a combination of dextro- and laevo-tartaric acid, is partially decomposed into its constituents by the simple act of solution. An analogous case of easy dissociation is furnished by nitrogen peroxide, N_2O_4, which is broken up very readily by heat.

Whether the polymeride thus found in tartaric (and malic) acid is a true chemical compound or a physical compound, it is not altogether easy to say, for the distinction is in general somewhat indefinite ; but, since it is radically different from any known crystalline modification, and appears to be comparatively simple, the former view seems much the more probable. In solutions of other substances molecular aggregations certainly exist, as is shown by the thermal experiments previously mentioned, but do not exhibit any radical change of physical properties such as is here found.

The theory throws some light on the effect of solvents. One cannot fail to notice that those liquids in which tartaric acid is

[1] Krecke, Archives Néerlandaises **7**, 107.   [2] Comptes Rendus **78**, 713.

difficultly soluble (acetone, etc.), are the ones which most diminish its rotation. In other words, those substances which do not facilitate dissociation by affording a ready solvent medium, allow molecular aggregations to produce the most marked effects. How far this may be able to account for the action of solvents on optically active substances in general remains yet to be seen. The same reasoning certainly holds for malic acid.

One other important fact must not remain unnoticed in the consideration of these acids. Each of them exists in more isomeric forms than can be accounted for by any theory yet advanced. Of tartaric acid there are the two active forms and two well-known inactive forms, while Staedel has shown[1] that the inactive tartaric acid obtained from glyoxal differs from the others. Even van't Hoff's hypothesis, usually so liberal with isomerides, accounts for but three forms (Die Lagerung der Atome im Raume, 37), and here are five.

With malic acid the case is much the same. There are two active forms, and probably three inactive forms, described by Bremer,[2] Pasteur[3] and Loydl.[4]

Racemic acid seems to be very closely related to the other inactive acids. Now, in racemic acid there is good reason to believe the molecule to be made up by a combination of right and left-handed molecules. If we consider how a dextro- and a laevo-form may be thus united and produce optical inactivity, it seems quite probable that they must be arranged with reference to a plane of symmetry. Considering now a body containing an asymmetrical carbon atom, and existing in dextro- and laevo-forms, the probability appears that such forms may be united each to each symmetrically to a plane, in four, and only four, different ways.

May it not be, that the unexplained isomerides of racemic acid, and the corresponding malic acid, which we believe to be combinations of right and left forms, differ from each other only in position with reference to their common plane of symmetry?

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[1] Ber. der deut. chem. Ges. **11**, 1752.   [2] Ber. d. deut. chem. Ges. **13**, 351.
[3] Ann. de Ch. et de Ph. (3) **34**, 46.   [4] Liebig's Annalen **192**, 80.

REVIEWS AND REPORTS.

A Method for the Quantitative Separation of Chlorine and Bromine.—E. Berglund.[1]

The method is based upon the fact that a mixture of acid sulphate and permanganate of potassium will liberate all of the bromine in a bromide, but cannot decompose a chloride ; and that the bromine thus liberated can be completely removed from an aqueous solution by means of a rapid current of air.

The apparatus consists of the following parts : an absorption bulb containing dilute caustic soda (1 to 50); a small flask in which the mixture of chloride and bromide is placed ; a small bottle for the dilute solution of permanganate (1 to 50) ; and a glass tube filled with cotton wool, through which the air necessary for the removal of the free bromine is filtered. The bottle for the permanganate and the flask in which the decomposition is effected are connected by means of a glass tube which extends to the bottom of each ; so that by lowering or raising the bottle, air or permanganate, as may be desired, can be introduced into the decomposing flask.

The substance to be analysed is placed in the flask, dissolved in 50 cc. of water, and treated with 15 to 25 cc. of a solution of acid sulphate of potassium (1 to 10); an aspirator is then attached to the absorption bulb, and a quantity of the permanganate solution drawn over into the mixture of bromide, chloride and acid sulphate. The bottle containing the permanganate is then lowered, and air rapidly drawn through the apparatus ($\frac{1}{3}$ liter per minute) until all of the bromine has been transferred to the absorption bulb. The hypobromite formed during the absorption of the bromine is decomposed by ammonia. The excess of permanganate in the solution of the chloride is reduced by means of alcohol.

The quantity of material taken should not exceed one gram, and the bromine should be completely removed within one and one-half hours. If more than one gram is taken, the solution is too concentrated and some chlorine is liberated. It is not safe to dilute the larger quantity by adding more water, since the time required for the removal of the bromine depends upon the volume of the liquid from which it is to be removed; and if more than one and a half hours are consumed in removing the bromine, some of the chloride is decomposed.

[1] Zeitsch. für anal. Chemie **24**, 184.

If, owing to the minuteness of the quantity of bromide, it is necessary to work with more than a gram of the mixture, the substance is dissolved in 15 to 25 cc. of water, and treated in the manner already described. The absorption bulb will then contain all of the bromine and a little chlorine. But these can be perfectly separated by reducing the hypobromite by means of ammonia, neutralising with sulphuric acid, and then subjecting the solution to the same treatment as the original material.

If the quantity of chlorine is very small, the permanganate should be added in small portions, and after each addition the liberated bromine should be removed. In this case there is no danger that any of the chlorine will be carried over with the bromine. The method is especially adapted to the determination of small quantities of bromine in the presence of large quantities of chlorides; as, for instance, in sea water.

A New Method for Determining Nitrogen in Organic Compounds.—J. Kjeldahl.[1]

This method, which is applicable to all compounds except those which contain the nitrogen in an oxidised condition or in the form of cyanogen, depends upon the fact that when a nitrogenous substance is heated with strong sulphuric acid and then oxidised with permanganate of potassium, the whole of the nitrogen is converted into the sulphate of ammonium.

The details of the method are as follows: One gram of the substance is weighed into a flask having a capacity of about 100 cc. Ten cc. of concentrated sulphuric acid (free from ammonia) are added. The flask is then placed upon a wire gauze and the contents heated nearly to the boiling point. The substance chars and the liquid presents the appearance of tar, but if the heating is continued for 1 to 2 hours the acid liquid will again become almost colorless. When this stage has been reached, finely pulverised potassium permanganate is sprinkled into the flask. Owing to the violence of the oxidising action it is best to add small portions of the permanganate in rapid succession. When the solution has assumed a green color, sufficient permanganate has been added, and the contents of the flask are allowed to cool. By this treatment the nitrogen will have been completely converted into ammonium sulphate, and it will only be necessary to decompose it with caustic soda. For this purpose the acid liquid is transferred to a flask of about 750 cc. capacity. The flask is provided with a rubber stopper, having an outlet tube which inclines upwards and connects with a spiral condensing worm. The lower end of the condenser enters a small Erlenmeyer flask, containing a measured quantity of standard acid solution. About 40 cc. of a solution of sodium hydroxide, free from ammonia and of 1.3 specific gravity,

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[1] Zeitsch. für anal. Chemie **22**, 366.

are added to the sulphuric acid solution, and the ammonia estimated in one of the usual ways.

The author analysed a large number and variety of compounds and obtained very excellent results.

The method is simple, accurate and expeditious. The author made fourteen determinations in a single day without assistance, and with sufficient apparatus the number could have been increased to twenty.

The Kjeldahl method for determining nitrogen in organic substances has been thoroughly tested and compared with the Varrentrapp-Will method by Heffter, Hollrung and Morgen.[1] The results obtained are highly satisfactory. The maximum limit of error in some 400 determinations made by the new method was .07 per cent. The method is fully as accurate as the soda-lime process, and possesses many advantages over the latter. These advantages are that it is much less expensive, and being much simpler in execution it permits of great economy in time. It is not necessary to have the substance to be analysed in a state of fine subdivision, and for liquid substances it is by far the most convenient. They have found it advantageous to treat 1 gram of the substance with 20 cc. of a mixture of 4 volumes concentrated sulphuric acid and 1 volume of fuming sulphuric acid. Two grams of phosphorus pentoxide are then added, and the operation carried on as recommended by Kjeldahl. They have also devised apparatus which facilitates the making of a large number of determinations simultaneously.

Petri and Lehmann[2] have found the new method of Kjeldahl to be admirably adapted to the determination of nitrogen in urine. 5 to 10 cc. of the urine, according to its concentration, are treated with 10 cc. of a mixture of concentrated sulphuric and fuming sulphuric acids, and subsequently oxidised with permanganate as directed by Kjeldahl. The authors publish the results of numerous analyses which establish the great accuracy of the method.

It is also strongly recommended by Bosshard.[3]

A Source of Error in the Determination of Nitrogen.

V. Meyer and Otto Stadler[4] found while making analyses of volatile organic sulphur compounds by the Dumas method that a considerable quantity of carbon monoxide collects with the nitrogen in the eudiometer. Especially is this the case when the combustion is rapid. The authors think it probable that the sulphur dioxide at first formed during the rapid combustion of organic substances rich in sulphur, reduces the carbon dioxide in the presence of the heated copper spirals. The carbon monoxide

[1] Zeitschrift für analytische Chemie **23**, 553. Chemiker Zeitung **8**, 432.
[2] Zeitschrift für physiologische Chemie **8**, 200.   [3] Zeitsch. für anal. Chemie **24**, 199.
[4] Berichte der deutschen chemischen Gesell. **17**, 1576.

then passes over with the nitrogen, and the results obtained are therefore too high. By passing a mixture of sulphur dioxide and carbon dioxide over heated metallic copper, small quantities of carbon monoxide were obtained. It is therefore recommended in making determinations of nitrogen in volatile organic sulphur compounds by Dumas' method, to carry on the combustion very slowly, and to have a long layer of lead chromate in the front part of the combustion tube. The measured gas should also be tested for the presence of carbon monoxide.

On the Detection of Nitrogen in Organic Compounds.—C. Graebe.[1]

The author has found that the Lassaigne method for detecting nitrogen in organic compounds is not universally applicable. The method consists in heating the compound with metallic potassium, and then treating a solution of the cyanide thus formed with a mixture of ferrous and ferric compounds. The formation of Prussian blue indicates the presence of nitrogen in the compound tested. Graebe has found that the diazo-compounds in general do not give this reaction, and he thinks it probable that the nitrogen escapes as a gas before any cyanide is formed.

A Simple Method for the Quantitative Determination of Nitric Acid.—Wildt and Scheibe.[2]

The Tiemann-Schulze method for determining nitric acid has several sources of error, which may produce unreliable results. The nitric oxide, which is measured over water, is not entirely insoluble; and, unless the water has been previously boiled, it contains oxygen, which will convert a portion of the nitric oxide into nitric and nitrous acids. The consequence of these facts is that the method tends to give too low results. The authors have modified the process by passing the nitric oxide through a solution of sodium hydroxide, to remove all traces of hydrochloric acid from the gas, and then into a flask containing air and water. · The nitric oxide is thus oxidised and dissolves in the water present. At the end of the operation the acid liquid is titrated with a standard alkali. The quantity of nitric acid is found at once, thereby avoiding the readings of temperature and barometric pressure as well as the calculations, which are necessary when the nitric oxide is measured.

Phosphorus. Method for Determining Phosphoric Acid Volumetrically.—O. von der Pforten.[3]

The phosphoric acid is precipitated with ammonium molybdate. The precipitate is thoroughly washed with an almost saturated solution of ammonium sulphate until all excess of ammonium

[1] Berichte der deutschen chem. Gesell. **17**, 1178.
[2] Zeitschrift für analytische Chemie **23**, 151.
[3] Zeitschrift für analytische Chemie **23**, 422.

molybdate has been removed. It is then dissolved in dilute ammonia, and the solution diluted to a definite volume. A measured portion, which should contain at least .3 gram MoO_3 and not exceed 30 cc. in volume, is taken for titration. 50 to 60 cc. of dilute hydrochloric acid and 8 to 10 grams of tin in sticks are added. The reduction is effected rapidly. The molybdenum present is reduced to the condition of suboxide, and the solution assumes a clear yellow color. The excess of tin is removed by filtration, and the solution then titrated with standard potassium permanganate. The suboxide is thus oxidised to sesquioxide, and from the quantity of permanganate used the quantity of molybdic acid present can be readily calculated. It was found that a constant relation exists between the proportions of phosphoric and molybdic acids present in the yellow ammonium phosphomolybdate, which is represented by 24 molecules of MoO_3 to one molecule of P_2O_5. The method gave good results, and is applicable in all cases in which phosphoric acid is separated by means of ammonium molybdate.

A New Method for the Qualitative Separation of Tin, Antimony and Arsenic.—E. Berglund.[1]

If a solution of the sulphides of tin, antimony and arsenic in sodium sulphide be boiled with copper oxide, the tin, antimony and arsenic will be converted into sodium stannate, sodium antimoniate and sodium arseniate, respectively. The copper oxide is best obtained by finely pulverising the granular oxide, which is prepared by igniting the nitrate. After treating the alkaline solution of tin, antimony and arsenic with copper oxide, the cuprous sulphide which is formed is removed by filtration, and to the filtrate $\frac{1}{4}$ to $\frac{1}{3}$ its volume of alcohol is added.

If antimony is present it will be precipitated. In the filtrate from the antimony precipitate the alcohol is expelled by boiling, and ammonium chloride added in excess. A milk-white precipitate indicates the presence of tin. If only a little tin is present no precipitate will be formed. Into the solution, in which a precipitate may be suspended, sulphuretted hydrogen is passed until the precipitate is dissolved. If no precipitate was present, the sulphuretted hydrogen is passed into the solution for only a short time. The solution is then made alkaline with ammonia, and the arsenic precipitated with magnesia mixture. The ammonium magnesium arseniate is filtered off, and the tin in the filtrate precipitated by hydrochloric acid.

A New Reagent for Sodium, Ammonium and Lithium.— H. Hager.[2]

When sodium, ammonium, or lithium salts are treated with a solution of potassium stannosochloride, a white precipitate is pro-

[1] Berichte der deutsch. chem. Gesell. **17**, 95.   [2] Pharm. Centralh. **25**, 289.

duced. The reagent is prepared by adding a solution of caustic potash, of 1.145 specific gravity, to a mixture of 5 parts of stannous chloride and 10 parts of distilled water until the solution has become almost perfectly clear. After allowing it to stand one hour, 5 parts of potassium hydroxide and 15 parts of distilled water are added. The reagent must be clear and colorless before it is used ; and all excess of free acid, in the solution to be examined, must be neutralised with caustic potash. If compounds of the earths or metals are present, they must be removed by pure potassium carbonate before using the reagent. Boracic acid prevents the precipitation of sodium salts ; but precipitation of lithium is not affected by it. •

A New Method for the Separation of Copper and Cadmium.—P. Gucci.[1]

To the solution from which bismuth has been precipitated by excess of ammonia, and which still contains copper and cadmium, dilute hydrochloric, nitric or sulphuric acid is added until the hydroxides of both metals have been dissolved. A slight excess of a solution of ammonium benzoate (10 per cent.) is then added and the copper precipitated as copper benzoate. The cadmium may then be detected in the filtrate by means of ammonia and ammonium sulphide. When only a small excess of ammonium benzoate is added, the separation is so perfect that the method may be advantageously employed in quantitative analysis. The precipitated copper benzoate is collected upon a filter, and, after washing, it is dried and ignited in a crucible. The reduced copper is then oxidised with nitric acid and weighed as oxide.

Separation of Nickel and Cobalt.—Ilinski and Knorre.[2]

If a solution containing nickel and cobalt and free hydrochloric acid be treated with nitroso-β-naphthol, all the cobalt will be precipitated as cobalt nitroso-β-naphthol, while the nickel will remain in solution.

To the solution containing a mixture of nickel and cobalt sulphates or chlorides add a few cubic centimeters of hydrochloric acid. To the warm solution add a hot solution of nitroso-β-naphthol in 50 per cent. acetic acid and allow the precipitate to settle. When a further addition of nitrosonaphthol solution no longer produces a precipitate, the solution is filtered and the precipitate washed with a 12 per cent. solution of hydrochloric acid. To the dry precipitate a little pure crystallised oxalic acid is added. It is then ignited in a Rose's crucible in a current of hydrogen. The cobalt is weighed in the metallic state. In the filtrate the nickel is precipitated with potassium hydroxide, after the acetic acid has been removed by boiling, and finally weighed as metallic nickel.

H. N. M. and E. H. K.

[1] Berichte der deutschen chem. Gesellschaft **17**, 2659.   [2] *Ibid.* **18**, 699.

The Manufacture of "Acid" Phosphates.

The manufacture of the so-called "Acid" Phosphates of commerce is generally considered to be rather a rule-of-thumb process. One is supposed to mix so much rock and acid and get such and such results. It is not often that even the chemist who is consulted by the manufacturer cares to enter largely into the details of the actual mixing. If he finds that the product does not come up to what the manufacturer desires, he generally contents himself with advising an increase of acid, or, what amounts to the same thing, a decrease of rock. If 80 per cent. of acid is not enough, 82 per cent. or 84 per cent. is recommended, and if that is not enough, then 86 per cent. or even 87½ per cent. But it is possible with ordinary Charleston Rock to calculate beforehand what the analysis should be. I say with ordinary Charleston Rock, for if the rock contains notable quantities of iron or aluminum the question is very much complicated. The ordinary Charleston Rock contains very small quantities of these troublesome substances, and for all practical purposes we may regard the phosphoric acid as existing in the form of tricalcium phosphate (bone phosphate). It certainly simplifies the question if we can assume that the initial reaction is the conversion of tricalcium phosphate into monocalcic phosphate and calcium sulphate by means of sulphuric acid.

I have undertaken some investigations into the nature of the phosphoric acid compounds formed immediately upon treating ordinary Charleston Rock with sulphuric acid. The rock was ground so that it entirely passed a 60° seive, it was then sampled, and submitted to a partial analysis, as only the moisture, silica, phosphoric acid, carbonic acid, iron, aluminum and lime were determined.

Two separate investigations were made, Nos. 1 and 2.

	I.	Analysis of rock used.
Moisture,	. . . . .	6.52 per cent.
Insol. silica,	. . . . .	17.84
Sol. "	. . . . .	.10
Phosphoric acid,	. . . .	22.82
Carbonic "	. . . .	2.80
Peroxide of iron,	. . . .	11.56
Oxide of aluminum,	. . .	.00
Lime,	. . . . .	33.60

The content here of iron is larger than usual.
Formula for making "acid" phosphate from this rock:

	lbs.
Rock, ...	1200
Sulphuric acid 47°B.	1050

Temperature of acid added 60° C. (140° F.), stirred 3 minutes.
Temperature in pan just before discharging 82° C. (180° F.)

Sample taken from pan just before discharging, put into bottle, closely corked, and cooled immediately. Analysed at once.

	Found.	Calculated.
Moisture,	27.75 per cent.	24.51 per cent.
Phos. acid sol. in water,	8.53	9 33
" " insol. in water,	2.92	2.84
" " sol. in. am. cit. 65°,	1.15	
" " insol. " " "	1.77	
" " total,	11.45	12.17

In regard to the method employed for calculating the analysis beforehand, it is simple and easily understood by any one possessing even a slight knowledge of the principles of chemical reactions. But at the outset a supposition has to be made which, although supported by evidence of great weight, still can not yet be taken as entirely authorised. This supposition is that the initial reaction goes on according to the formula:

$$Ca_3P_2O_8 + 2H_2SO_4 = CaH_4P_2O_8 + 2CaSO_4.$$

Assuming then that this is the reaction, let us see what follows therefrom. 100 lbs. of $Ca_3P_2O_8$ containing 45.81 lbs. P_2O_5 require 200 lbs. of H_2SO_4 of 53°B. (or *exactly* 53.1°B.) for complete decomposition into $CaH_4P_2O_8$ and $CaSO_4$. 200 lbs. 53°B. acid = 229 lbs. 47° B. The 100 lbs. $Ca_3P_2O_5$ contain 45.81 lbs. P_2O_5, so that to render soluble in water 1 lb. P_2O_5 there is needed 5 lbs. 47° B. acid, or 1 lb. 47° B. renders soluble .20 lb. P_2O_5. The rock used contained 22.82 per cent. P_2O_5; 1200 lbs. were used in the mixture, so that we have 273.84 lbs. P_2O_5 to render soluble. We require, therefore, 1369.20 lbs. 47° B. acid if we wish to make all of the phosphoric acid soluble in water. We actually used 1050 lbs. 48° B. acid, and as each pound of this renders soluble .20 lb. P_2O_5, we should have in the whole mixture of 2250 lbs. 210 lbs. P_2O_5 soluble in water, or 9.33 per cent.

As regards the P_2O_5 insoluble in water:

We should have used 1369.20 lbs. 47° B.; we actually used 1050 lbs., so that the difference between what we should have used and what we did use multiplied by the soluble-coefficient (if I may use the term), which in this case is .20, represents the P_2O_5 we might have made soluble, but did not ($1369.20 - 1050) \times .20 = 63.84$ lbs. P_2O_5 insoluble in water = 2.84 per cent.

It will be seen from a comparison of the "found" and "calculated" percentages that there is a difference of .80 per cent. between the two "solubles," and one of .72 per cent. between the two "totals," the excess in both cases being on the side of the "calculated." As regards the two "moistures," the excess in the "found" may be accounted for by some carbonic and hydrofluoric acids being driven off by drying, and counted hence as "moisture."

All things considered, the agreement between the "found" and the "calculated" is close enough for all practical purposes.

The better grades of Charleston Rock do not contain as much oxide of iron as this sample, and it is likely that it affects the P_2O_5 sol. in water, so that we might expect to find less "soluble" than is given by calculation.

Experiment No. 2 was conducted with a better rock than No. 1.

Experiment No. 2.

Analysis of rock used:

Moisture,	2.32 per cent.
Insol. silica,	11.56
Sol. "	.14
Phosphoric acid,	26.29
Carbonic "	3.33
Peroxide of iron,	3.35
Oxide of aluminum,	3.07
Lime,	38.55

Formula for mixing:

Rock (60 mesh)	1500 lbs.
Sulphuric acid 46° B.,	1200

Temperature of acid added 50° C. (122° F.), stirred 3 minutes.
Temperature in pan just before discharging 71° C. (160° F.)

Sample taken from pan just before discharging, put into bottle, closely corked, and cooled immediately. Analysed at once.

	Found.	Calculated.
Moisture,	22.45 per cent.	21.73 per cent.
Phos. acid sol. in water,	8.81	8.73
" " insol. in water,	5.01	5.87
" " sol. in am. cit. 65°	1.69	
" " insol. " " "	3.32	
" " total,	13.82	14.60

It will be remembered that both these analyses represent the acid phosphate at the very moment of discharging from the mixer. It is of the utmost importance to the manufacturer to ascertain what are the changes, if any, which take place in the article between the moment of mixing and the moment of selling. Let us suppose that 250-500 tons are made by formula No. 2 and dumped in a large pile, and let us further suppose that analysis No. 2 represents fairly the condition of the article when first made. What will the analysis be at the end of one week, or one month? It is impossible to say exactly what are the changes that go on, they are very complicated, and are determined by numerous conditions, no one of them clearly understood.

A lot of 250 tons made by formula No. 2, and with the same rock, gave, 3 days after mixing, the following analysis:

Moisture, ... 16.72 per cent.
Soluble phosphoric acid, . . 9 34
Phosphoric acid insoluble in water, 5.69
"   " soluble in am. cit. 65°, 3.52
"   " insol.   "   "   " 2.17
Total, ... 15.03

The temperature of the pile being 100° C. (212° F.) at the time of taking sample. As Wagner has remarked (in his Dünger-fabrikation, p. 60), the composition of the superphosphate varies according to the composition of the crude phosphate used, the quantity of sulphuric acid employed, and very considerably according to the manufacturing process. There are so many things that influence the composition of the superphosphate, and the so-called " acid " phosphate, that to investigate them all requires much time and patience. It is sometimes surprising to see what a great difference in the product a small change in the formula can determine. The addition of 50 lbs. of water often causes variations not at all to be anticipated, while the humidity of the atmosphere is a point not to be overlooked. In another article I desire to discuss the chemical reactions that are begun and continued in the manu-facturing and storing of " acid " phosphates. The old notion that the gain in " reverted " phosphoric acid is determined by the causes that affect the loss of " soluble " is not sustained by the facts in the case. (See my article on the " The Reversion of Phosphoric Acid in 'acid' and superphosphates made from Red Navassa Rock," Journ. Elisha Mitchell Soc. 1884, and Shepard and Robertson's recent admirable pamphlet on " The changes that occur in heaps of acid phosphate.") In the present state of knowledge it is hardly possible to say what those changes are.

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THE COMPOSITION AND EXAMINATION OF THE COMMERCIAL SULPHATE OF QUININE.[1]

The majority of chemists agree in representing the composition of the crystallised sulphate of quinine by the formula $(C_{20}H_{24}N_2O_2)_2$ $H_2SO_4 + 7H_2O$. But the commercial sulphate is never pure, it always contains sulphate of cinchonidine, as it is impossible to separate these sulphates by recrystallisation from water.

The ordinary examination consists merely in the estimation of the water, and the detection of the presence of the cinchonidine by

means of the well-known reactions of Hesse and de Kerner, or by ether. Now since the value of the commercial article depends solely upon the quantity of quinine it contains, it is very desirable that this should be estimated. For this purpose three methods are available: first, that of Vrij, in which the quinine is determined in the form of sulphate of iodoquinine (herapathite). This method gives accurate results. The second consists in the separation of the alkaloids by means of ether. This has not given good results, because the two alkaloids combine with each other. The third and best method is the optical, which consists in practice in determining the specific rotatory power of a mixture of the tartrates by Oudemans' method.

Assuming a certain degree of concentration A as a standard, Oudemans found for the pure tartrate of quinine, $[\alpha]_D = -215°.8$, and for the pure tartrate of cinchonidine, $[\alpha]_D = -131°.3$. The author of this paper, adopting Oudemans' standard of concentration A, examined nine specimens of the commercial sulphate of quinine, and obtained specific rotatory powers varying from $-209°.84$ to $-203°.78$. A single sample gave him $-192°.42$. The quantity of tartrates obtained, after applying the correction for the part which remained dissolved, was from 95.77 to 91.86 per cent. The pure sulphate of quinine with seven molecules of water should give 93.58 per cent.

The composition of the nine specimens was therefore:

Sulph. of quinine,	95.11	92.20	91.30	90.13	88.92	87.74	87.10	84.32	72.03
" " cinchonidine,	6.87	5.47	9.52	9.29	10.15	12.92	11.79	13.44	26.25
	101.98	97.67	100.82	99.42	99.07	100.66	98.89	97.76	98.28

According to Oudemans' experiments, the errors made in these estimations, using the Laurent polarimeter, are very small. The use of the tartrates also causes a slight error, which, however, has but little influence on the final result.

The author, having concluded from theoretical considerations that it was impossible to separate a mixture of the sulphates of quinine and of cinchonidine by repeated crystallisations from water, assured himself of the correctness of this conclusion by polarimetric experiments, which showed that though the quantity of cinchonidine became smaller it never entirely disappeared. It is only by preparing the acid sulphate, $C_{20}H_{24}N_2O_2, H_2SO_4, 7H_2O$, or the hydrochloride, $C_{20}H_{24}N_2O_2, HCl, 2H_2O$, that the two alkaloids can be separated. By afterwards transforming these salts into tartrates they can be shown by the polarimeter to be free from cinchonidine.

The tartrate and oxalate, like the normal sulphate, cannot be purified by recrystallisation from water. On account of this property the author points out that the two alkaloids are monacid. They give with bibasic acids double salts containing both alkaloids

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at the same time, and these double salts differ in their properties
from the simple salts.

While, according to Oudemans, the tartrate of quinine contains
one molecule of water and that of cinchonidine two, the author
finds from his own experiments that the double salt crystallises
with one molecule of water. These experiments follow :

1. A mixture of air-dried tartrates, prepared from a commercial
sulphate of quinine, gave at 17° C., concentration A (Oudemans),

$$[a]_D = -205°.3,$$

from which the composition is calculated to be :

87.6 per cent. tartrate of quinine with one mol. of water,
12.4   "   "   "   cinchonidine with two mol. of water.

The same tartrates lost 2.3 per cent. of water on heating to 125°–
130° C. for eight hours in a paraffin bath. Assuming that these
two tartrates were the ones with which we had to deal, the calcu-
lated loss would have been 2.5 per cent. water; while if we suppose
that all the cinchonidine is in the form of the double salt and that
this double salt contains only one molecule of water, the calculated
loss would be 2.22 per cent., which is much nearer the quantity
found.

2. A mixture of tartrates prepared in the same manner, but with
another sample of sulphate of quinine, gave

$$[a]_D = -206.°81,$$

from which the composition is calculated to be :

89.4 per cent. tartrate of quinine with one mol. of water,
10.6   "   "   "   cinchonidine with two mol. of water.

The loss of water on heating was 2.21 per cent. Calculating on
the first supposition it should be 2.46 per cent., on the second
2.219 per cent.

3. A mixture of tartrates prepared from a commercial sulphate
of cinchonidine gave

$$[a]_D = -140.°15,$$

from which we obtain :

10.46 per cent. tartrate of quinine with one mol. of water,
89.54   "   "   "   cinchonidine with two mol. of water.

The loss of water was 4.09 per cent. Calculating on the first
supposition it should be 4.374 per cent.; assuming that all the
quinine is in the form of the double tartrate, 4.18 per cent.

As has already been stated, the author concludes from these
results that the mixture of tartrates contains a double tartrate of
quinine and cinchonidine, slightly soluble in water.

The accuracy of the polarimetric determination is greater if the
specific rotatory power be calculated from the anhydrous salts.
The specific rotatory power for the concentration A is then found

to be for the pure anhydrous tartrate of quinine $-220°.07$, and for the pure anhydrous tartrate of cinchonidine $-137°.67$, and the formula for calculating the quantity of anhydrous tartrate of quinine in one hundred parts,

$$220.07x + 137.67 (100 - x) = 100 [a]_D m.$$

But the influence of this correction upon the final result is very slight, as may be seen from the following cases :

A specimen of commercial sulphate of quinine gave 90 per cent. of air-dried tartrate, containing 2.3 per cent. of water ; the 90 parts therefore contain 87.93 parts of anhydrous tartrate.

For the crystallised salt the specific rotatory power was

$$[a]_D = - 205°.3,$$

and for the anhydrous salt,

$$[a]_D = - 210°.13.$$

From the formula for the crystallised salt,

$$215.8x + 131.3 (100 - x) = 100 \times 205.3,$$

we find that the crystallised tartrates are composed of :

87.6 per cent. tartrate of quinine with one mol. of water.
12.47   "   "   " cinchonidine with two mol. of water.

The 90 parts of crystallised tartrates therefore contain :

78.9 tartrate of quinine $= 62.66$ quinine $= 84.32$ sulphate of quinine ;

11.1 tartrate of cinchonidine $= 8.52$ cinchonidine $= 11.39$ sulphate of cinchonidine.

From the formula for the anhydrous tartrates,

$$220.07x + 137.67 (100 - x) = 100 \times 210.13,$$

we find :

87.9 per cent. anhydrous tartrate of quinine,
12.1   "   "   cinchonidine ;

hence for the 87.93 parts :

77.29 tartrate of quinine $= 62.76$ quinine $= 84.46$ sulphate of quinine.

10.64 tartrate of cinchonidine $= 8.49$ cinchonidine $= 11.16$ sulphate of cinchonidine.

The difference of 0.1 in the quinine and 0.03 in the cinchonidine is not very great.

There has often been some uncertainty about the quantity of water of crystallisation of the normal sulphate of quinine, which is not the case with the acid sulphate nor the hydrochloride. The author thinks that the chemists who have estimated this water have used a sulphate of quinine containing some double sulphate of quinine and cinchonidine, and that this double sulphate contains

six molecules of water.   In this case the pure sulphate of quinine crystallises with eight molecules of water, as Hesse assumes, and as is shown by Flückiger and Robiquet.

Method for Rapid Estimation of Urea.

Being called upon to make a good many brief and rapid analyses of urine on " clinic days " of our medical department, I devised the following modification of Knop's method of estimating urea, and after using it for a year with perfectly satisfactory results, venture to describe and recommend it as especially adapted for physicians' use, by reason of simplicity, cheapness and accuracy.   In perfecting and testing it I was assisted greatly by J. Torrey, Jr., then working with me.
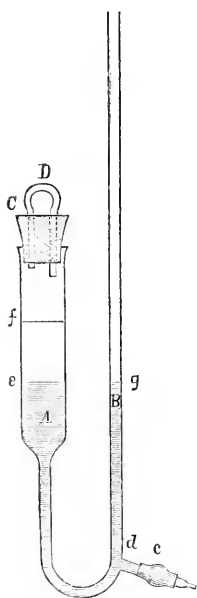
The apparatus consists of the glass tube A, which is about 8 cm. long and $2\frac{1}{2}$ cm. in diameter, joined to the tube B, which is about 25 or 30 cm. in length in its longer arm and 8 or 10 in its shorter, and has a diameter of about 5 mm.   Near the bend is an outlet tube c, provided with " ball valve " or pinch cock. d, e, f, g, are marks upon the tubes. C is a rubber cork with two holes through which the bent tube D passes. D is of such size and length as to hold about 1 cc., and one of its ends may be a trifle longer, that the other.

The apparatus is used as follows : Remove the cork and pour in mercury until it stands at e and g, then fill up to the mark f with sodium or potassium hypobromite (made by shaking up bromine with a strong solution of sodium or potassium hydroxide).   Next carefully fill the tube in the cork with the urine, being careful especially not to run it over or leave air bubbles in it.   This can easily be done by using a small pipette, but if accidentally a little runs over it should be wiped off the end of the cork with blotting paper.   The cork is then to be inserted closely into the tube, the urine tube being so small the urine will not run out in so doing.   The mercury is then drawn out through c till it stands in B at d. Its level in A will of course not be changed greatly.   Now, incline the apparatus till the surface of the hypobromite touches the urine in the longer part of the urine tube and then bring it upright again.   The urine will thus be discharged into the hypobromite, which will of course decompose the urea, liberating nitrogen, which will cause the mercury to rise in B.   Shake till no further change of level is seen, and mark the level of mercury in B with a rubber band, then remove the cork,

draw out the liquid with a pipette, dry out the tube above the mercury with scrap of blotting paper, pour back the mercury drawn out, and repeat the process to be sure that no error was made.

If now, two or three marks have been made upon the tube *B*, indicating the height of the mercury when solutions containing known per cents. of urea are used, an accurate opinion can be at once formed as to the condition of the urine as regards urea.

As is well known, normal urine contains about 2.5–3 per cent. of urea, so that graduations representing 2, 2.5, 3, and 4 per cents. are usually all that are needed, though of course many more can be easily made.

The results obtained with this apparatus have been repeatedly compared with those of more elaborate ones, and no practical difference observed. Evidently the same apparatus, differently graduated, might be employed to determine the carbonate present in such a substance as crude soda ash or other similar mixture. In such a case the weighed material would be put upon the mercury with water and the small tube filled with acid.

<div align="right">F. C. ROBINSON.</div>

BOWDOIN COLLEGE CHEMICAL LABORATORY.

Note on the Determination of Carbon Monoxide.[1]

It has been noticed by those who have used palladium chloride for the quantitative determination of carbon monoxide in gaseous mixtures (especially in air) where the proportion of CO is small, that the reaction takes place very slowly. Welitschkowsky,[2] for example, found that a series of from 3 to 5 Geissler bulbs was necessary for the complete absorption of the carbon monoxide and other reducing gases in mixtures of illuminating gas and air, and Fodor[3] found that air containing 1 volume of carbon monoxide in 1000 could not be safely passed through or over the absorbing solution more rapidly than at the rate of from 150 to 200 cc. per hour.

We have found that—since the gas must remain in contact with the solution for a certain length of time—additional security is gained by using mushroom-shaped flasks, which afford a large absorption surface, and by passing the gas in an intermittent stream. By the aid of an aspirator a partial vacuum is first established in the flask containing the palladium chloride ; this is then filled with the gaseous mixture, and after the gas has remained in the first flask for 20 minutes, it is allowed to pass into a second and then into a third. All of the CO may be absorbed in the first flask, the others are added to afford security. This operation as described is a slow one, as much as 8 hours being

[1] Communicated by Prof. W. R. Nichols.   [2] Archiv für Hygiene **1** (1883), 231.
[3] Vierteljahrsschrift für öffentliche Gesundheitspflege **12** (1880), 397.

sometimes required for a liter of air. We have found, however, that if the solution of palladium chloride is kept at a temperature of from 80° to 90° C., the reaction is complete at the end of 5 minutes, and a liter of air containing as much as 8 volumes of the monoxide in 1000, or as little as can be estimated at all, may be passed through a series of the smaller flasks in an hour and a half or through the larger flasks in half an hour. Working at this temperature we have experienced no difficulty from the formation of a basic salt.

The " mushroom-shaped flasks " are simply the show-glasses or show-bottles which are sometimes used in museums, especially for the display of seeds, etc. These are inverted and furnished with stoppers and conducting tubes; our larger ones have a diameter of about six inches, a depth (inside) of about an inch and a half in the center, and a capacity of about 375 cc.; the smaller ones have a capacity of about 100 cc.

It may be further noted that in titrating with potassium iodide it is essential that the solution of palladium chloride be made somewhat acid, as is clearly stated by Fodor. Welitschkowsky's statements as to the difficulties of the titration can be understood only on the supposition that this point was overlooked by him.

ELLEN H. RICHARDS.

On the Solubility of the Sulphides of Copper and Zinc in Melting Potassium Sulphide, and on their Insolubility in Melting Sodium Carbonate and Nitrate.

Some finely pulverised pyrites were melted in a covered porcelain crucible with an equal weight of potassium carbonate and half its weight of sulphur, the melted mass treated with hot water and the solution filtered. From this solution, when acidulated with hydrochloric acid, *all* the metallic substances dissolved were separated together with sulphur as sulphides in form of a brownish yellow precipitate, which, when after drying extracted with bisulphide of carbon, left a dark brown residue. This residue, melted with a mixture of sodium carbonate and nitrate, left, when extracted with water, a black powder soluble in hydrochloric acid, with green color. Sulphuretted hydrogen gave a precipitate with this solution; the brown deposit formed contained besides copper sulphide a small amount of lead sulphide, and the filtrate from it furnished, after addition of ammonia and ammonium sulphide, zinc sulphide. The solution separated from the black powder (see above) *did not contain any copper or zinc*, but traces of lead and small traces of arsenic. A quantitative determination of the above sulphides gave the following amount:

Copper sulphide 2.52 per cent. of the quantity of pyrites taken.
Zinc   "   0.64   "   "   "
Lead   "   0.0056   "   "   "

EDO CLAASSEN.

AMERICAN

CHEMICAL JOURNAL.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.[1]

By W. A. Noyes.

II.

Whether ortho-brom-toluene can be oxidised by potassium ferricyanide in alkaline solution or not, was left undecided by the experiments described in my first paper. I have now repeated the experiments, using for the purpose pure ortho-brom-toluene, and find that it can be oxidised to ortho-brom-benzoic acid by the agent in question. The oxidation, however, takes place with great difficulty.

The ortho-brom-toluene was prepared from ortho-toluidine by the method described by Jackson.[2] The ortho-toluidine used was obtained from Schuchardt in Goerlitz, and gave, on heating in a sealed tube with glacial acetic acid, an acettoluid which fused at 107°. The crude ortho-brom-toluene at first obtained was heated on the water-bath for five hours with a mixture of potassium bichromate, sulphuric acid and water. After separating from the oxidising mixture it was distilled from a solution of caustic potash with water vapor.

The oxidation was conducted as described in my first paper. One gram of the ortho-brom-toluene with a mixture of 25 grams of potassium ferricyanide, 12 grams of caustic potash and 100

grams of water were boiled for three or four hours with an inverted condenser. The unoxidised brom-toluene was then distilled with water vapor. The solution left was filtered from ferric oxide, which always separated, the filtrate was evaporated somewhat, and part of the potassium ferrocyanide was crystallised out. The crystals of ferrocyanide were filtered off and washed once or twice with cold water. The filtrate and washings were acidified with hydrochloric acid and extracted with ether. The ether was distilled off, the residue was dissolved in a little ether, and the solution evaporated on a weighed watch-glass. The residues obtained in this way in three different experiments weighed, respectively, 4.3, 5 and 3.9 milligrams. The residues obtained by the oxidation of para-brom-toluene under the same conditions weighed in two experiments 6.4 and 6.5 milligrams.

Of course these residues cannot be considered as pure in either case, but the results obtained indicate that ortho-brom-toluene is oxidised more slowly than para-brom-toluene, by potassium ferricyanide.

In order to obtain enough of the ortho-brom-benzoic acid to establish its existence in the residues mentioned above, six grams of ortho-brom-toluene were oxidised in lots of one gram each. The acid obtained was converted into the barium salt and the solution of the salt was evaporated to dryness. The residue was treated with alcohol and filtered, the filtrate was evaporated to dryness, the residue dissolved in a little water, and the ortho-brom-benzoic acid precipitated with hydrochloric acid and recrystallised from water. It fused at 144°–145°, hence lacked a little of being perfectly pure. However, under the circumstances there could be no reasonable doubt as to its identity, and it was not thought profitable to spend further time on this point. The presence of bromine in the acid was established by qualitative tests.

Oxidation of para-toluene-sulphamide.

In studying the oxidising action of chromic acid on benzene derivatives, Remsen and his colleagues have found the sulphamide derivatives especially suitable for the purpose, on account of the properties of the acids obtained by their oxidation. It was thought desirable, accordingly, to include some of these substances in the study of the oxidising action of potassium ferricyanide.

The para-sulphamide of toluene was prepared from toluene in

the usual way by conversion into the sulphonic acid and successive treatment of the potassium salt of the latter with phosphorus penta-chloride and ammonia. After crystallising from water the amide fused at 136°.

Two grams of the amide were boiled for three hours with 20 grams of caustic potash, 50 grams of potassium ferricyanide and 200 cc. of water. The filtrate from the ferric oxide was concentrated and part of the potassium ferrocyanide crystallised out. On acidifying the filtrate from the ferrocyanide with hydrochloric acid, a precipitate of para-sulphamine-benzoic acid, mixed with unoxidised toluene-sulphamide, was obtained. The solution of the barium salt obtained by boiling with barium carbonate was evaporated to dryness, and the residue was treated four times with strong alcohol to remove the sulphamide still mixed with the salt. The purified salt was then dissolved in hot water, filtered, and the filtrate cooled quickly. The salt separated in peculiar ball-like masses. These were separated from the mother liquors, washed slightly, and allowed to stand loosely covered for two days till air-dry. The salt was analysed with the following results:

0.2103 gram of the salt lost 0.0309 gram H_2O at 160°, and gave 0.0770 gram $BaSO_4$.

		Calculated.	Found.
$(C_7H_6SO_4N)_2$	400	63.80	...
Ba	137	21.85	21.53
$5H_2O$	90	14.35	14.69

The purified barium salt obtained by a second oxidation conducted in the same manner as the first, was dissolved in water and the acid precipitated with hydrochloric acid. The acid was recrystallised from water and analysed.

0.1567 gram of the acid gave 0.01141 gram N (Frankland's method).

	Calculated for $C_7H_7SO_4N$.	Found.
N	6.97	7.28

The acid was nearly insoluble in cold water, and soluble with difficulty in hot water. It began to fuse with decomposition at about 280°.

A rough estimate of the yield was made with the second oxidation. From two grams of para-toluene-sulphamide there was obtained by precipitation from the purified barium salt about 1.1 grams of the acid.

The analyses given above could leave no doubt that para-sulphamine-benzoic acid is formed by the oxidation of para-toluene-sulphamide with potassium ferricyanide. However, as Remsen[1] reports in his analysis of the barium salt of this acid *one* molecule of water instead of *five*, as found by myself, I thought best to oxidise some of the para-amide in the manner described by him,[2] with potassium bichromate and sulphuric acid, and make a more careful study of the barium salt of the acid obtained in that way.

The oxidation was conducted exactly as described by Remsen. After converting into the barium salt, the solution of the latter was evaporated to dryness, and the residue was treated several times with strong alcohol to remove any unoxidised amide which it might contain.

On crystallising from water some difficulty was found in obtaining salts of definite composition. It was finally established that if a hot solution of the salt was allowed to stand still so that no crystals were formed, until it was cold, a salt separated in ball-like masses containing five molecules of water ; on the other hand, if the salt crystallised out while the solution was still warm, the crystals were in the form of small scales with a pearly lustre and contained two molecules of water. It was found that the salt with five molecules of water lost a large part of its water quite rapidly on standing over sulphuric acid. The last portions of the water were given off more slowly, but the salt became almost anhydrous by long standing (one month) over sulphuric acid. In all probability this is the salt which Remsen prepared, and on drying it over sulphuric acid he happened to leave it just long enough so that all but one molecule of water was given off.

The analyses of the salts were as follows :

0.1265 gram of the salt which separated from the cold solution lost 0.0185 gram H_2O at 180°, and gave 0.0474 gram $BaSO_4$.

	Calculated.	Found.
Ba	21.85	21.88
$5H_2O$	14.35	14.51

I. 0.1697 gram of the salt which crystallised in scales from a warm solution lost 0.0108 gram H_2O at 170°, and gave 0.0692 gram $BaSO_4$.

[1]Annalen der Chemie **178**, 302.   [2]*Ibid.* **178**, 297.

II. 0.1302 gram of the salt lost 0.0084 gram H_2O at 170°, and gave 0.0524 gram $BaSO_4$.

	Calculated.	Found. I.	Found. II.
Ba	23.91	23.98	23.65
H_2O	6.28	6.36	6.45

OXIDATION OF META–NITRO–TOLUENE.

By W. A. Noyes and W. E. Moses.

In the experiments described by one of us it was shown that both ortho- and para-nitro-toluene are quite easily oxidised by potassium ferricyanide and caustic potash, while toluene itself is oxidised with great difficulty. In other words, the nitro group when in the ortho or para position with reference to the methyl of toluene, causes that methyl to be very much more easily attacked by this oxidising agent. The question whether a nitro group in the meta position with reference to the methyl would have the same effect was naturally suggested. The experiments here described were undertaken to determine that point.

The meta-nitro-toluene was prepared from para-toluidine. This was converted into para-acettoluid by heating in sealed tubes for two hours with twice the weight of glacial acetic acid. The temperature used was 150°-160°, and the yield was almost quantitative. The nitro group was introduced as described by Cosack.[1] Ten grams of the para-acettoluid were put in a flask with 45 grams of glacial acetic acid, and a little more than the calculated amount of nitric acid, sp. gr. 1.50 or above, was added. It was found that if the acetic acid contained a little water, or if the nitric acid was a little weaker, the nitration was unsuccessful. The meta-nitro-para-acettoluid was recrystallised from water. The acetyl group was split off by boiling with caustic potash, and the amido compound was recrystallised from alcohol.

The amido group was eliminated as described by Goldschmidt.[2] The meta-nitro-toluidine was suspended in absolute alcohol, and nitrous anhydride was passed in until the odor of nitrous ether was strongly marked. The diazo compound formed was decomposed by heating on the water-bath, and the excess of alcohol and nitrous

[1] Berichte der deutschen chemischen Gesellschaft **13,** 1088.   [2]*Ibid.* **11,** 1625.

ether were distilled off. The meta-nitro-toluene was then distilled over in a current of steam. It was redistilled once or twice in the same way to purify it. Thus prepared it solidified on cooling nearly to 0°, and melted again at 16°.

For the purpose of a more exact comparison the oxidation of ortho- and para-nitro-toluene was repeated. The para-nitro-toluene used was obtained from Kahlbaum and fused at 54°. The ortho-nitro-toluene was prepared from para-toluidine by nitrating as recently described by Nölting and Collin.[1] It was found that a sulphuric acid of 66° B. (= sp. gr. 1.767), as directed in the article referred to, did not answer nearly so well as a stronger acid of sp. gr. 1.835. The amido group was eliminated by the same method which was used for the meta compound.

The comparison of the oxidation of the three nitro-toluenes was conducted as follows : About one gram of each nitro-toluene was boiled for three hours with a mixture of 25 grams of potassium ferricyanide, 10 grams of caustic potash, and 100 cc. of water. The unoxidised nitro-toluene was then distilled over in a current of steam. The solution was filtered and the filtrate evaporated till quite concentrated. When cold the potassium ferrocyanide which crystallised out was filtered off, and the crystals washed till the filtrate and washings amounted to 70 cc. The filtrate was acidified with 5 cc. of concentrated sulphuric acid diluted with an equal volume of water. It was then extracted three times with ether, using about 20 cc. each time. The ethereal extract was allowed to evaporate spontaneously in a weighed platinum dish, and the residue was dried over sulphuric acid till the weight was constant.

The residue obtained in this way by the oxidation of one gram of ortho-nitro-toluene was 0.69 gram ; that obtained from one gram of para-nitro-toluene was 0.73 gram, while that obtained from one gram of meta-nitro-toluene was 0.052 gram. In another experiment with meta-nitro-toluene two grams were boiled for three hours with twice the amount of the oxidising mixture used above. The residue obtained weighed 0.087 gram, and 1.67 grams of unoxidised nitro-toluene were recovered.

Of course these numbers are no exact measure of the relative ease with which the three nitro-toluenes are oxidised. In the case of the meta compound the amount of the nitro-toluene in contact with the oxidising mixture must have been nearly the same from

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[1] Berichte der deutschen chemischen Gesellschaft **17**, 263.

the beginning to the end of the experiment; with the ortho and para compounds, on the other hand, the nitro-toluene had nearly disappeared at the end of three hours. Further, the residues could not have been quite pure nitro-benzoic acid in either case, and the impurities would be likely to form a larger per cent. of the small amount of meta-nitro-benzoic acid than of the large amounts of the ortho and para acids. However, the experiments prove beyond question that while ortho and para-nitro-toluene are oxidised readily and in nearly equal amount by the mixture we are studying, meta-nitro-toluene is oxidised with great difficulty— with greater difficulty, indeed, than toluene itself.

In order to obtain enough of the meta-nitro-benzoic acid for analysis more than a dozen oxidations were made. In all, 400 grams of potassium ferricyanide were used. The acid obtained was converted into the barium salt. After two crystallisations the salt was nearly pure, the acid obtained from a portion of it fusing at $137°-138°$. A small portion of the salt, after boiling with bone-black and recrystallising, gave an acid fusing at $140°-141°$. The analyses were made with the less pure salt, but with three different sets of crystals. The salt used for the third analysis had stood a day longer than the others, and was probably slightly effloresced, as meta-nitro-benzoate of barium loses its water very easily.

The analyses were as follows:

I. 0.0613 gram of the salt lost 0.0080 gram H_2O at $150°$.

II. 0.0584 gram of the salt lost 0.0076 gram H_2O at $150°$, and gave 0.0245 gram $BaSO_4$.

III. 0.0629 gram of the salt lost 0.0080 gram H_2O at $150°$, and gave 0.0271 gram $BaSO_4$.

	Calculated.		Found.	
		I.	II.	III.
Ba	25.32	...	24.68	25.34
$4H_2O$	13.31	13.05	13.01	12.72

If we take the same view of the conduct of meta-nitro-toluene, which has ordinarily been taken of the conduct of ortho compounds toward chromic acid, it would seem to follow that a nitro group in the meta position with reference to a methyl group protects the latter from oxidation by potassium ferricyanide and caustic potash. A consideration of the conduct of toluene and the brom-toluenes toward the same oxidising agent leads to a different conclusion.

Their conduct seems to indicate that it is not so much that a nitro group in the meta position *protects* a methyl group, as that a nitro group in the ortho or para position has, as it were, a *loosening* effect on a methyl group, causing the latter to be more easily attacked by the oxidising agent which we are studying. The sulphamide group in the para position seems to have much the same effect as the nitro group.

A somewhat similar effect of the nitro group has already been noticed by Körner.[1] He found that when a nitro group is in the ortho or para position with reference to a halogen atom, the latter can be easily exchanged for an amido or a hydroxyl group by boiling with alcoholic ammonia or potash. If the nitro group is in the meta position such an exchange cannot be effected by that means.

It seems probable from the results of the experiments described that we have discovered in potassium ferricyanide and caustic potash a means of oxidising a methyl group which is ortho to a nitro group, leaving a second methyl in the meta position untouched. Such an agent has been hitherto unknown.

University of Tennessee, *May 19th*, 1885.

ON BENZOYLACETIC ACID AND SOME OF ITS DERIVATIVES.[2]

Part I.

By W. H. Perkin, (Jun.), Ph.D., *Privatdocent at the University of Munich.*

Among the many methods which have been discovered and employed in the last few years, for the synthesis of organic compounds, those which are based on the use of acetoacetic ether are among the most important, this body being useful in two ways for building up organic bodies : in the first place, on account of the acid character of the hydrogen-atoms contained in the methylene-group ; and in the second place, being a ketone, it is capable of entering into almost all the reactions which characterise the latter

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[1] Jahresberichte, 1875, 365.   [2] Communicated by the Author.

class of bodies. The replacement of the hydrogen-atoms in aceto-acetic ether, by alcohol and acid radicals, has been especially studied by Wislicenus and his pupils ; whereas the reactions which involve the ketone-group have, with few exceptions, been more or less neglected.

The reason of this is that not only are the experimental difficulties great, but there is also considerable uncertainty in interpreting the results, owing to the mobility of the different groups in aceto-acetic ether. More especially does doubt exist as to the part played by the methyl-group in such reactions and condensations. For this reason it appeared to me that it would be very interesting to carefully examine the benzoylacetic ether, recently discovered by Baeyer,[1] with especial reference to reactions in which the ketone-group takes part. Benzoylacetic ether, as was to be expected, gives in the aromatic series bodies exactly corresponding to those obtained from acetoacetic ether in the fatty series, and for this reason, as well as on account of the stability of the benzoyl-group, and the greater tendency of bodies in the aromatic series to crystallise, it seemed to be especially adapted to the study of the more complicated condensations.

Before entering into the details of this research, I should like to express my sincere thanks to Professor Baeyer, in whose laboratory it was carried out, for his kind help and advice which he always placed at my disposal during its progress, as well as for the interest which he took in all my other studies. I must also thank Herr C. Bernhart for the help which he gave me in the experimental part.

Part I of this research comprises the preparation and properties of benzoylacetic ether, benzoylacetic acid, and the compounds in which the hydrogen-atoms in the methylene-group are replaced by alcohol radicals.

Preparation of Phenylpropiolic Acid.

Cinnamic acid, as is well known, combines directly with two atoms of bromine, being thereby converted into phenyldibromo-propionic acid, thus :

$$C_6H_5.CH : CH.COOH + Br_2 = C_6H_5.CHBr.CHBr.COOH.$$
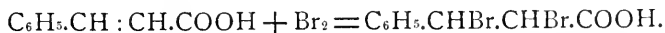
This acid, on treatment with alcoholic potash, first gives up 1

[1] Ber. **15**, 2705.

mol. of hydrobromic acid, forming the two isomeric α- and β-monobromocinnamic acids according to the equation—

$$2C_6H_5CHBr.CHBr.COOH = C_6H_5CBr : CH.COOH$$
$$\text{\small α-Monobromocinnamic acid.}$$
$$+ C_6H_5CH : CBr.COOH + 2HBr.$$
$$\text{\small β-Monobromocinnamic acid.}$$
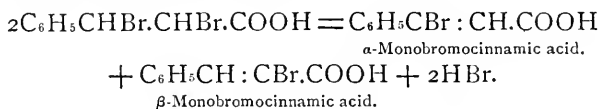
By converting these acids into ammonia salts and recrystallising once or twice from water, it is easy to separate the one from the other, the ammonia-salt of α-monobromocinnamic acid being much less soluble than that of the β-acid. Of these two bodies only the α-acid gives a good yield of phenylpropiolic acid on treatment with alcoholic potash, the β-acid being partly transformed into monobromostyrolene and other secondary products.[1] It is therefore necessary, before heating with potash, to transform the β-acid into the α-acid, which is easily done by heating it some degrees above its melting point, or more simply still by etherification, in which case the ether of the α-acid is formed. The formation of phenylpropiolic acid from α-monobromocinnamic acid is represented by the following equation :

$$C_6H_5.CBr : CH.COOH = C_6H_5.C \vdots C.COOH + HBr.$$
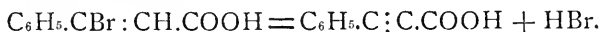
After many experiments, however, it was found that the following modification of the above process gives the best results, at the same time rendering the somewhat troublesome transformation of the β- into the α-monobromocinnamic acid unnecessary.

500 grams of cinnamic acid are suspended in about 1–$1\frac{1}{2}$ litres of absolute alcohol, and hydrochloric acid is passed through till the whole is dissolved and the liquid is thoroughly saturated with the gas. The product, after standing for two or three hours, in order to make sure that the reaction is complete, is poured into ice and water, and the oil which sinks to the bottom is separated by means of a tap funnel, the watery liquid being extracted with a little ether. This oil, which consists of almost pure cinnamic ether, is next dissolved in a little ether, washed with a dilute solution of sodium carbonate, to remove traces of hydrochloric acid and unchanged cinnamic acid ; and after thoroughly drying over chloride of calcium, treated with 440 grams of bromine, in small quantities at a time, care being taken to keep the liquid cool. The bromine disappears instantly without evolution of hydrobromic acid. After

[1] Barisch, J. pr. Chem. [2], **20**, 180; Glaser, Annalen, **154**, 140.

standing for a short time, the whole is poured into a large open dish and the ether allowed to evaporate, when phenyldibromo-propionic ether separates out in large crystals, forming a solid cake at the bottom of the dish. The crystals are then separated from the mother-liquor, pressed between filter-paper, exposed to the air for a short time to remove traces of bromine, and lastly, if necessary, crystallised from ligroin or alcohol.

The mother-liquor on evaporation deposits crystals of the ether, which are somewhat discolored by impurities, but on recrystallisation may easily be obtained pure, and melting at 69°.

A weighed quantity of this body is now added to the calculated quantity of alcoholic potash (1 mol. of ether requires 3 mols. of potash). The reaction is so energetic that the heat evolved is generally sufficient to cause the alcohol to boil. As soon as all the ether has been added, the whole is heated to boiling for six to eight hours in a flask connected with an inverted condenser. After distilling off the alcohol, the residue, which consists of a mixture of potassic phenylpropiolate and potassic bromide, is dissolved in water and filtered, and the clear liquid is acidulated with an excess of dilute sulphuric acid, which precipitates the phenyl-propiolic acid as an oil, which, however, on standing, soon solidifies,

Phenylpropiolic Acid.
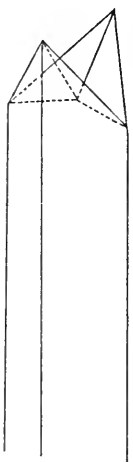
especially if well agitated from time to time. The crude acid is next filtered off, well washed with water, dissolved in carbonate of soda solution, and gently heated with animal charcoal for about half an hour on a water-bath, agitating well from time to time. After filtering off the animal charcoal, an almost colorless solution of soda-salt is obtained, which, on acidulating with sulphuric acid, deposits the phenylpropiolic acid nearly pure. If required perfectly pure, it must be crystallised from water, and is thus easily obtained in well-characterised crystals, which Professor Haushofer was kind enough to measure and describe as follows :

" Prismatic crystals of the rhombic system with monoclinic habit. Acute dihedral angle of the prism 66° 50'. Of pyramidal faces, there appear constantly only the pair resting on an obtuse edge

of the prism. Very characteristic is the twin-combination of the crystals according to the macropinacoid, whereby the hemi-

pyramids of the two individuals are symmetrically joined, and form re-entering angles. The entire development of the crystals is so decidedly monoclinic, that my reference of them to the rhombic system is based solely on the directions of extinction on the prismatic faces, which directions are exactly parallel and perpendicular to the prismatic edges."

Phenylpropiolic acid is produced from the dibromophenylpropionic ether according to the following equation :

$$C_6H_5.CHBr.CHBr.COOC_2H_5 + 3KOH = C_6H_5.C \vdots C.COOK + 2KBr + 2OH_2.$$
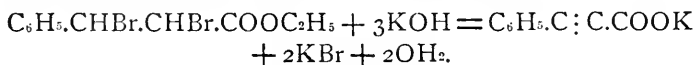
By this method there is apparently no bromstyrolene formed, and if care be taken to avoid any large excess of potash in saponifying the dibromophenylpropionic ether, the yield is very good, about 80–85 per cent. of the theoretical amount. If, however, excess of potash be used, the phenylpropiolic acid is easily decomposed into phenylacetylene and acetophenone.

Preparation of Benzoylacetic Ether.

The phenylpropiolic acid must now be converted into the ethylic ether, which is best done in the following way. Pure phenylpropiolic acid is dissolved in absolute alcohol, and hydrochloric acid gas is passed through the liquid till the whole is thoroughly saturated, care being taken to cool the liquid well during the operation, after which the product is left at rest for two or three hours in order to complete the reaction. The whole is then poured into ice-cold water, and the phenylpropiolic ether, which is precipitated as an oil, is two or three times extracted with ether.

The etheric solution, after washing with dilute carbonate of soda, is well dried over chloride of calcium and the ether is distilled off, when pure phenylpropiolic ether remains behind as a thick, and almost colorless oil, having a fruity smell and burning taste ; it does not solidify at 0°. If rubbed on the skin it produces a most painful burning sensation. When quickly distilled it boils between 260° and 270° without undergoing much decomposition. When this ether is dissolved in common sulphuric acid it takes up the elements of water, forming ethylic benzoylacetate, thus :

$$C_6H_5.C \vdots C.COOC_2H_5 + H_2O = C_6H_5.CO.CH_2.COOC_2H_5.$$
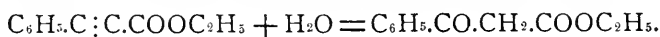
For the formation of benzoylacetic ether in this way, commercial sulphuric acid is somewhat too concentrated, and a better yield is obtained if a few drops of water are added to every kilogram before use.

The method of preparation is the following: From 2 to 3 kilos. of sulphuric acid are cooled to 0° in a freezing mixture, and then 100 grams of phenylpropiolic ether are slowly added, drop by drop, so that the temperature never rises above $+ 3°$, the whole being well shaken after each addition. The sulphuric acid becomes colored slightly brownish during the reaction, and there appears always to be a little sulphurous anhydride formed, especially if a rise of temperature takes place. After standing for two or three hours at as low a temperature as possible, the product is slowly poured on powdered ice, everything being carefully cooled, and the operation being best performed by allowing the sulphuric acid to trickle into a funnel filled with ice, which is kept well stirred all the time. The watery liquid, which is filled with drops of oil, is repeatedly extracted with ether. The etheric solution is then quickly washed with a dilute solution of sodium carbonate, and finally dried over potassium carbonate, which, as a rule, extracts a quantity of coloring matter. After filtering from potassium carbonate and distilling off the ether, crude benzoylacetic ether remains behind as a thick yellowish oil.

In order to purify this liquid, it is next shaken with a cold dilute solution of caustic soda and a little animal charcoal, and filtered, the whole operation being performed as quickly as possible, in order to avoid decomposition of the ether. The clear alkaline solution is next mixed with ice, acidulated with dilute sulphuric acid, and well shaken with ether; and lastly, this etheric solution is carefully dried over potassium carbonate, and the ether distilled off, when pure benzoylacetic ether remains behind as a colorless oil, which can easily be freed from traces of ether by leaving it for some time over sulphuric acid in a vacuum.

On analysis the following numbers were obtained:

I. 0.2072 gram substance gave 0.1198 OH_2 and 0.5208 CO_2.

Found.	Theory, $C_6H_5.CO.CH_2COOC_2H_5$.
C $= 68.62$ per cent.	68.75 per cent.
H $= 6.42$	6.25
O $= 24.96$	25.00

Benzoylacetic ether is a colorless oil having an agreeable smell, somewhat recalling that of acetoacetic ether. It does not solidify at 0°. If quickly fractioned most of it distils over between 265° and 270° without much decomposition. Under a pressure of 200 mm. it passes over between 230° and 235°. It should not, however, be distilled, if this operation can be avoided, as it entails considerable loss, and the crude ether is generally pure enough for most purposes.

Benzoylacetic ether is sparingly soluble in water, but mixes with ether and alcohol in all proportions. The solution in alcohol gives the same violet coloration with chloride of iron as acetoacetic ether. By boiling with water, or better with dilute sulphuric acid, it is split up into acetophenone, alcohol, and carbonic anhydride, according to the equation:

$$C_6H_5.CO.CH_2.COOC_2H_5 + H_2O = C_6H_5CO.CH_3 + CO_2 + C_2H_5OH.$$
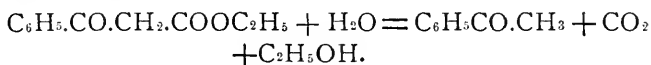
This decomposition is exactly analogous to the splitting up of acetoacetic ether into acetone, alcohol, and carbonic anhydride. In benzoylacetic ether, just as in acetoacetic ether, the hydrogen-atoms in the CH_2-group are replaceable by sodium. It appears, however, that after having replaced 1 atom of hydrogen with sodium, it is necessary first to exchange this for some radical such as ethyl, before it is possible to insert another.

The sodium compound is best prepared by mixing benzoyl-acetic ether (4 grams) with a strong solution of sodium ethylate in alcohol, containing the calculated quantity of sodium (0.6 gram). The reaction takes place according to the equation:

$$C_6H_5.CO.CH_2.COOC_2H_5 + NaOC_2H_5 = C_6H_5.CO.CHNa. COOC_2H_5 + C_2H_5OH.$$
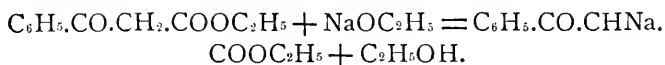
After standing for some time in the dark, the sodium-compound crystallises out in long silky needles, which, however, on being exposed to the air, quickly turn brown, especially when moist.

The mother-liquor is then drawn off by means of a vacuum pump, and the crystals are pressed between filter-paper, when the sodium-compound is obtained pure, having somewhat the appearance of cotton-wool. On standing in contact with the air, however, it slowly decomposes. If heated in the dry state it decomposes easily, yielding acetophenone and other bodies. It is readily soluble in water and alcohol, almost insoluble in ether.

The following derivatives of benzoylacetic ether were prepared by precipitation from a solution of the sodium-compound in water.

The *barium compound*, $(C_{11}H_{11}O_3)_2Ba$, is precipitated on adding barium acetate as a white amorphous mass, sparingly soluble in water, but more so in alcohol.

The *silver compound*, $C_{11}H_{11}AgO_3$, is formed by adding a solution of silver nitrate. It is a white amorphous precipitate. On warming, silver is immediately precipitated; it is also easily decomposed by caustic soda.

On adding copper sulphate to the solution of the sodium salt, the *copper compound*, $(C_{11}H_{11}O_3)_2Cu$, is precipitated as a pale green mass, insoluble in water. In dilute soda solution it dissolves easily, forming a beautiful blue solution, from which CuO is precipitated on boiling.

The *lead compound* is precipitated, on adding lead acetate, as a white precipitate, which is also soluble in caustic soda.

Ferric chloride gives a dirty violet coloration with dilute solutions of the sodium salt, the liquid becoming turbid on standing.

Benzoylacetic Acid.

Some time since Ceresole[1] by saponifying acetoacetic ether with dilute potash at ordinary temperatures, obtained the corresponding acetoacetic acid. It therefore appeared interesting to see if in this case, by saponification in the cold, benzoylacetic acid could be isolated, this appearing the more probable, as benzoylacetic ether is more stable than acetoacetic ether. Pure benzoylacetic ether was therefore dissolved in dilute aqueous potash ($2\frac{1}{2}$–3 per cent.), care being taken to avoid any large excess, and then left at rest at the ordinary temperature for about 24 hours. The product was then filtered, and after carefully cooling with ice, acidulated with dilute sulphuric acid, when the acid was precipitated in white flakes. After extracting with ether, the etheric solution was allowed to evaporate at the ordinary temperature, the acid remaining behind as a slightly brownish, hard, crystalline mass, which was next dissolved in dilute ammonia, shaken with a little animal charcoal, and filtered.

On acidulating with dilute sulphuric acid, and extracting with ether, the acid remained as an almost colorless crystalline mass, consisting of nearly pure benzoylacetic acid.

In order to obtain the body perfectly pure, it is dissolved in a little warm benzene (at 70°), and a trace of light petroleum added. On cooling, the acid crystallises out in small crystals, which, when seen under the microscope, appear in the form of thin transparent needles, which polarise light. The analysis gave the following numbers :

I. 0.1519 gram substance gave 0.0675 gram OH_2 and 0.3647 gram CO_2.

II. 0.1402 gram substance gave 0.0695 gram OH_2 and 0.3614 gram CO_2.

	Found.		Theory, $C_6H_5CO.CH_2.COOH$.
	I.	II.	
C =	65.48	66.06 per cent.	65.85 per cent.
H =	4.93	5.17	4.88
O =	29.59	28.77	29.27

Benzoylacetic acid, several times crystallised from benzene, melts at 103–104°, if quickly heated, at the same time undergoing decomposition, with evolution of carbonic anhydride. (The melting point, 85–90°, first given in the *Berichte* [16, 2129], is too low, owing to the fact that at that time I had not sufficient substance at my disposal to purify it by repeated crystallisation.)

The acid appears to sublime slowly at ordinary temperatures, so that if preserved in a test-tube, the sides, after some months, become covered with thin colorless transparent plates, consisting, apparently, of pure benzoylacetic acid. This acid is difficultly soluble in light petroleum, and crystallises from the hot solution on cooling in small flat needles. It is easily soluble in alcohol, ether and hot benzene. On adding light petroleum to the solution in benzene the acid is almost completely precipitated in the form of slender needles.

A small crystal of the acid dissolved in alcohol gives, on addition of a drop of ferric chloride, a beautiful reddish-violet coloration.

Benzoylacetic acid is sparingly soluble in cold water, the solution giving only a slight coloration on adding chloride of iron; it is much more easily soluble in hot water, a drop of chloride of iron producing an intense violet coloration.

Benzoylacetic acid may be formed directly, by dissolving finely powdered phenylpropiolic acid in concentrated sulphuric acid, according to the equation :

$$C_6H_5.C:C.COOH + H_2O = C_6H_5.CO.CH_2.COOH.$$
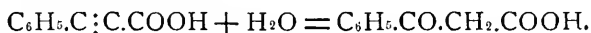
When the acid liquid is poured on ice, a yellow amorphous mass is obtained, consisting of benzoylacetic acid, mixed with a little unchanged phenylpropiolic acid.

The former acid, on heating either alone or with dilute sulphuric acid, is quantitatively decomposed into acetophenone and carbonic anhydride, thus :

$$C_6H_5.CO.CH_2.COOH = C_6H_5.CO.CH_3 + CO_2.$$
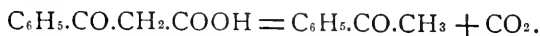
The formation of acetophenone, by the action of concentrated potash on phenylpropiolic acid, is probably due to the latter first taking up the elements of water, being thereby converted into benzoylacetic acid, which is then decomposed by the further action of the alkali into potassium carbonate and acetophenone.

Benzoylacetic acid dissolves easily on shaking with dilute soda, sodium carbonate, or ammonia. In order to prepare the silver salt, the acid was dissolved in dilute ammonia, and the solution, after filtering, left over sulphuric acid in a vacuum till the excess of ammonia had volatilised, or, better still, carefully neutralised with pure nitric acid. On adding a solution of silver nitrate, the silver salt was precipitated in the form of a white amorphous mass, somewhat soluble in water. It was filtered off, well washed, and dried over sulphuric acid in a vacuum. The analysis gave the following numbers :

0.1440 gram substance gave 0.0567 gram silver.

Found.	Theory, $C_6H_5CO.CH_2.COO Ag.$
$Ag = 39.37$ per cent.	39.77 per cent.

The silver salt is instantly decomposed on heating, with separation of silver.

The following salts were prepared from the ammoniacal salt, which can be obtained as a waxy crystalline mass, by allowing the aqueous solution to evaporate to dryness in a vacuum over sulphuric acid. The crystals are generally mixed with traces of acetophenone, produced by the spontaneous decomposition of the salt. The ammonium salt is easily soluble in water. On adding *ferric chloride* to a solution of the ammonium salt, a thick blackish-violet precipitate is formed, which is slowly decomposed on boiling, carbonic anhydride being evolved. *Ferrous sulphate* does not give any precipitate. The *copper salt* is produced by adding a solution of copper sulphate to a fairly concentrated solution of the

ammonium salt, as a light greenish-yellow precipitate, which is not formed in dilute solutions.   It is fairly stable, but is slowly decomposed on boiling.

The *lead salt* is precipitated, on adding acetate of lead, as a heavy white amorphous precipitate.   The calcium and barium salts are easily soluble in water.

The salts of benzoylacetic acid are difficult to obtain pure and to analyse, on account of their tendency to decomposition into acetophenone and carbonic anhydride.   From the above facts it is evident that benzoylacetic acid, although not a stable body, is much more so than acetoacetic acid, which has never been obtained pure enough for direct analysis.

Ethylbenzoylacetic Acid.

It was now necessary to see whether it was really possible, as in the case of acetoacetic ether, to replace the hydrogen atoms in the methylene-group, by alcohol-radicals, such as methyl, ethyl, etc., and thus to obtain higher homologues of benzoylacetic acid.   The first experiment tried was the action of ethyl iodide on the sodium-compound of benzoylacetic ether, in the hope of getting ethyl-benzoylacetic ether, according to the following equation :

$$C_6H_5.CO.CHNa.COOC_2H_5 + C_2H_5I = C_6H_5 + CO.CH(C_2H_5).$$
$$COOC_2H_5 + NaI.$$
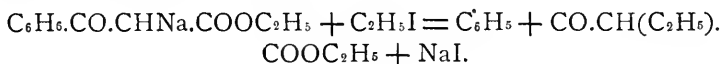
The method of procedure was the following :

0.6 gram of sodium was dissolved in about 15 cc. of absolute alcohol, and then mixed with 5 grams of pure benzoylacetic ether, taking care to avoid any rise of temperature.   10 grams of ethyl iodide were then added, and the whole heated on a water-bath till a sample, on dilution with water, had no longer an alkaline reaction. The alcohol and excess of ethyl iodide were then distilled off, the residue mixed with water, and the oily product extracted with ether.   The etheric solution, after well washing and drying over carbonate of potash, left, on distilling off the ether, a thick yellowish oil, consisting probably of nearly pure ethylbenzoylacetic ether, which was, however, not further examined, as it appeared to be decomposed on distillation.   In order to obtain the free acid, the oil was mixed with dilute alcoholic potash and left for several days at the ordinary temperature until, on diluting a sample with water,

only a small quantity of oil was precipitated. The product was mixed with water and several times extracted with ether, to remove any unchanged ethylic ethylbenzoylacetate. The solution of the potash salt of the new acid was then acidulated with dilute sulphuric acid, a solid acid being thereby precipitated, which was extracted with ether. After distilling off the ether, the acid remained behind as a semi-solid mass, which was first spread on a porous plate to remove traces of oil, and then purified by dissolving it in a small quantity of dilute alcohol, from which solvent it crystallises in small needles.

After drying at 60° the following numbers were obtained on analysis :

0.1914 gram substance gave 0.1082 H_2O and 0.4814 CO.

	Theory, $C_6H_5CO \atop C_2H_5 > CH.COOH.$
Found.	
$C = 68.60$ per cent.	68.75 per cent.
$H = 6.28$	6.25
$O = 25.12$	25.00

It was therefore ethylbenzoylacetic acid. The acid melts at 111–115° with slight decomposition, but could not be obtained free from traces of benzoic acid, which, while rendering it difficult to get an accurate melting point, do not much influence the analytical results. It is easily soluble in alcohol, ether, and benzene, and crystallises on evaporating the etheric solution in silky needles ; it is easily soluble also in ammonia, soda, and sodium carbonate solution. When warmed with dilute sulphuric acid it is decomposed, carbonic acid being given off, and an oil remaining behind, probably consisting for the most part of ethylacetophenone.

Decomposition-products of Ethylbenzoylacetic Ether.

It next appeared interesting to determine whether the substituted benzoylacetic ethers would, on heating with alcoholic potash, undergo the same decompositions as the corresponding substituted acetoacetic ethers, which, as is well known from the researches of Wislicenus, are split up in two ways. He found, namely, that on employing a highly concentrated potash solution, the product consisted chiefly of organic acids, whereas with dilute solutions a large amount of ketone and only a small quantity of organic acids were obtained, according to the following equations, taking ethylacetoacetic ether as example :

I. $CH_3.CO.CH(C_2H_5).CO_2C_2H_5 + 2KOH = CH_3.CO_2K +$
$$C_2H_5.CH_2CO_2K + C_2H_5OH.$$
Butyric acid.

II. $CH_3.CO.CH(C_2H_5).CO_2C_2H_5 + 2KOH =$
$$CH_3.CO.CH_2.C_2H_5 + C_2H_5OH + K_2CO_3.$$
Methylpropyl ketone.
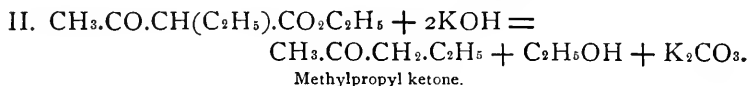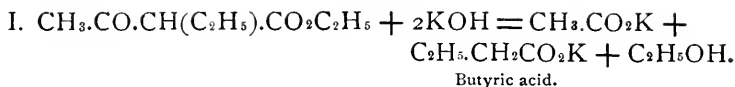
As will be seen from the following remarks, this rule applies also to the substituted benzoylacetic ethers.

In order to examine the decomposition-products of ethylbenzoylacetic ether, the crude ether was heated on a water-bath for three hours with moderately concentrated alcoholic potash. The mixture quickly became deep brown, and acquired a smell strongly resembling that of acetophenone. At the end of the reaction water was added, and the precipitated oil was separated from the potash-salt, by extraction with ether.

The etheric solution, after well washing with water, and drying with carbonate of potash, gave, on distilling off the ether, a dark brownish oil, which was then carefully fractioned. Almost the whole quantity distilled over by the first distillation, between 215–230°, and gave, on oft-repeated fractioning, an oil, boiling constantly at 220–222°.

The analysis gave the following results :

0.1588 gram substance gave 0.1140 gram H_2O and 0.4687 CO_2.

	Found.	Theory, $C_6H_5.CO.CH_2.C_2H_5.$
C =	80.49 per cent.	81.08 per cent.
H =	7.97	8.10
O =	11.54	10.82

Propylphenylketone had therefore been formed from the ethylbenzoylacetic ether by splitting off CO_2 and alcohol, according to the following equation :

$C_6H_5.CO.CH(C_2H_5)COOC_2H_5 + 2KOH =$
$$C_6H_5.CO.CH_2.C_2H_5 + C_2H_5OH + K_2CO_3.$$
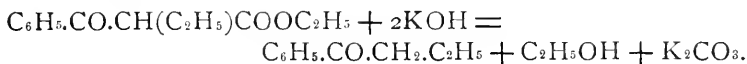
This ketone has already been described by Schmidt and Fieberg,[1] and by Burcker.[2] The former obtained it by the distillation of a mixture of benzoate and butyrate of lime, the latter by the action of aluminium chloride on butyric chloride and benzene.

[1] Ber. **6**, 498.   [2] Bull. Soc. Chim. **37**, 4.

It does not combine with sodium bisulphite. On oxidation with chromic acid and sulphuric acid, benzoic and propionic acids are formed.

In order to examine the acids produced by the action of potash on ethylbenzoylacetic ether, the potassium salt which has been separated from the propylphenylketone, by extraction with ether, was next acidulated with dilute sulphuric acid, and distilled with steam. An almost colorless but strongly acid liquid distilled over, which possessed strongly the characteristic smell of butyric acid. The residue on cooling was extracted with ether.

On distilling off the ether a solid acid remained behind, which crystallised from water in silky plates, possessing all the properties of benzoic acid. They melted at 120°, and sublimed very easily on heating, and gave the characteristic iron reaction : in order to be certain the acid was turned into the silver salt and analysed with the following result :

0.4026 gram substance gave 0.1917 gram $Ag = 47.59$ per cent.
Theory for $C_6H_5COOAg = 47.16$

By the action of potash on ethylbenzoylacetic ether, a second decomposition had therefore taken place, according to the following equation :

$$C_6H_5CO.CH(C_2H_5).COOC_2H_5 + 2KOH = C_6H_5COOK + CH_2(C_2H_5).CO_2K + C_2H_5OH.$$
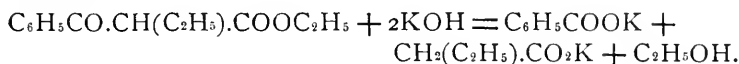
As in the case of substituted acetoacetic ethers, it was found on using very concentrated potash that mostly organic acids were formed, and that in order to get a good yield of phenylpropylketone it is advisable to use the alkali, moderately dilute, and to digest for a longer time.

Diethylbenzoylacetic Acid.

From the foregoing it is clear that one of the hydrogen-atoms in the methylene-group in benzoylacetic ether may be replaced by alcohol radicals, the result being the production of homologues of this ether, exactly corresponding in the aromatic series to the substituted acetoacetic ethers in the fatty series. It remained, however, to be tested whether the second hydrogen-atom could, in like manner, be replaced. *e. g.*, by ethyl, producing diethylbenzoylacetic ether. This, as a matter of fact, is the case. The experiment was carried out in the following way :

A mixture of 1.2 gram of sodium (dissolved in about 20 cc. of absolute alcohol), 10 grams benzoylacetic ether, and 10 grams ethyl iodide, was heated in a sealed tube for about three hours to 100°.

At the end of this time, the product having become neutral, the alcohol was distilled off, then 1.2 gram of sodium (dissolved as before in 20 cc. of absolute alcohol) added to the residue, and the whole was heated with 10 grams of ethyl iodide three or four hours to 100°.

The reaction takes place in two phases. In the first place, ethyl-benzoylacetic ether is formed, which is then further acted on by the sodium ethylate and ethyl iodide, forming diethylbenzoylacetic ether, according to the following equation :

$$C_6H_5.CO.C(C_2H_5)Na.COOC_2H_5 + C_2H_5I =$$
$$C_6H_5.CO.C(C_2H_5)_2.COOC_2H_5 + NaI.$$
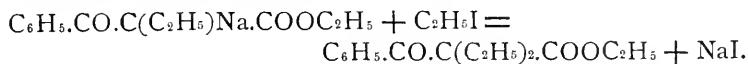
At the end of the reaction the alcohol is distilled off, the residue diluted with water, and extracted several times with ether. After distilling off the ether the diethylbenzoylacetic ether remains behind as a thick dark-brown oil, which, as it could not be purified by distillation, was directly saponified and the acid examined.

For this purpose the ether was dissolved in alcohol, and after adding very dilute alcoholic potash, allowed to stand for some weeks at ordinary temperatures. The product was then diluted with water, and any unsaponified diethylbenzoylacetic ether removed by extracting several times with ether. On acidulating the solution of the potash salt with dilute sulphuric acid, an oily acid was precipitated, which, on standing for some time and continually stirring, became quite solid. It was once or twice extracted with ether, and the ethereal solution dried over calcium chloride. On distilling off the ether, diethylbenzoylacetic acid remained behind as a brownish crystalline mass, which was spread on a porous plate to remove traces of oil. The acid, which was now only slightly yellowish colored, was purified by dissolving in dilute ammonia and agitating with animal charcoal. On filtering and acidulating with dilute sulphuric acid, the acid was obtained in the form of an almost colorless crystalline solid. Although the saponification was conducted at ordinary temperatures, and with very dilute potash, the diethylbenzoylacetic acid always contained traces of benzoic acid, which spoilt the analytical numbers and melting point.

0.2121 gram substance gave 0.1325 gram H_2O and 0.5417 gram CO_2.

Found.	Theory $C_6H_5.CO.C.(C_2H_5)_2.COOH$.
C = 69.66 per cent.	70.90 per cent.
H = 6.94	7.27
O = 23.40	21.81

The acid melts at 128–130°. Heated either alone or with dilute sulphuric acid, it gives off carbonic anhydride, and an oil is left behind, probably diethylacetophenone.

Diethylbenzoylacetic acid is easily soluble in ammonia, soda, or sodic carbonate. On account of the difficulty of getting the acid pure, the salts were not further examined, it appearing probable that better results would be obtained on studying the decomposition-products of diethylbenzoylacetic ether.

Decomposition-products of Diethylbenzoylacetic Ether.

In order to examine these products, crude diethylbenzoylacetic ether was heated on a water-bath with dilute alcoholic potash for about five hours, by which means the ether was completely decomposed. After distilling off the alcohol and diluting with water, an oil was precipitated, which was separated from the solution of the potash salts by extracting with ether. The aqueous solutions were then gently warmed on a water-bath to get rid of the ether, acidulated with dilute sulphuric acid, and distilled in steam. A strongly acid, slightly turbid distillate came over, which smelt strongly of the higher members of the acetic series, and probably contained diethylacetic acid. The residue on cooling deposited an acid, in the form of feathery crystals, which were collected on a filter and washed with water. The acid crystallised from water in silky plates, which possessed all the properties of benzoic acid. They melted at 120°, and gave the characteristic reaction with ferric chloride. In order to be certain, the acid was turned into the ammonia salt and precipitated with silver nitrate. An analysis of the silver salt gave the following numbers:

0.2994 gram substance gave 0.1420 gram silver.

Found.	Theory C_6H_5COOAg.
Ag = 47.43 per cent.	47.16 per cent.

Diethylbenzoylacetic ether is therefore decomposed on heating with dilute alcoholic potash, partly into benzoic acid and diethylacetic acid, according to the equation:

$$C_6H_5.CO.C(C_2H_5)_2.COOC_2H_5 + 2KOH = C_6H_5.COOK +$$
$$CH(C_2H_5)_2.CO_2K + C_2H_5OH.$$
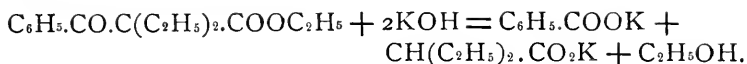
The neutral oils, produced by the action of potash on diethyl-benzoylacetic ether which had been separated from the potash salts by extraction with ether, were next examined. After drying over calcium chloride and distilling off the ether, a dark brownish oil remained behind, which was fractioned. The principal portion which distilled over between 220° and 235° gave, after several times carefully fractioning, an oil boiling constantly at 229–231° (at 710 mm.), which gave the following numbers on analysis, showing that diethylacetophenone had been formed :

0.1711 gram substance gave 0.1371 H_2O and 0.5099 gram CO_2.

Found.	Theory $C_6H_5.CO.CH(C_2H_5)_2.$
C $=$ 81.28 per cent.	81.81 per cent.
H $=$ 8.90	9.09
O $=$ 9.82	9.09

Diethylacetophenone is a thick colorless oil, which does not solidify at 0°, the smell of which closely resembles that of aceto-phenone. Bromine acts easily on the solution in glacial acetic acid, on warming, quantities of hydrobromic acid being given off. The product is a colorless oil, which was not further examined, as it could not be purified by distillation, owing to decomposition, and on standing for some weeks over sulphuric acid *in vacuo* it did not crystallise. The formation of diethylacetophenone by the action of potash on diethylbenzoylacetic ether may be expressed by the following equation :

$$C_6H_5.CO.CH(C_2H_5)_2.COOC_2H_5 + 2KOH =$$
$$C_6H_5.CO.CH(C_2H_5)_2 + K_2CO_3 + C_2H_5OH.$$
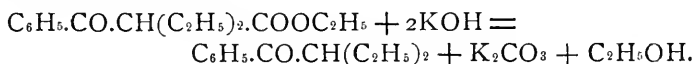
Allylbenzoylacetic Acid.

This acid and its decomposition-products were more especially examined, on account of their isomerism with benzoyltetramethy-lene-carbonic acid and benzoyltetramethylene obtained by the action of trimethylene bromide on benzoylacetic ether (an account of which I hope to give in a short time), it being for several reasons interesting to determine any differences which might exist between these two bodies. Allylbenzoylacetic ether was prepared by the action of allyl iodide on the sodium compound of benzoylacetic ether in the following way :

10 grams of benzoylacetic ether were mixed with 1.2 gram of sodium (dissolved in about 15 cc. of absolute alcohol), and the whole, after adding an excess of allyl iodide, heated on a water-bath for about four hours, or better still in a sealed tube to 100° for two hours, after which the mass had acquired a neutral reaction. The alcohol was then distilled off, the residue diluted with water, and several times extracted with ether. After drying over chloride of calcium and distilling off the ether, allylbenzoylacetic ether remained behind as a thick brownish oil, which, as it could not be distilled without decomposition, was not directly analysed.

In order to obtain allylbenzoylacetic acid, the crude ether was dissolved in alcohol, a little dilute alcoholic potash added, and the whole allowed to stand at ordinary temperatures for three weeks. The product was then diluted with water, and any unsaponified ether removed by extraction with ether.

The solution of the potash salts was then acidulated with dilute sulphuric acid, and once or twice extracted with ether. After distilling off the ether, the acid remained behind as a brownish crystalline mass, which was first roughly purified by spreading out on a porous plate.

In this manner the acid was obtained as a yellowish crystalline mass, which was very easily soluble in most of the ordinary solvents, and for this reason could not be satisfactorily recrystallised from any of them. It was therefore dissolved in dilute ammonia, and after shaking with animal charcoal and filtering, reprecipitated and analysed with the following result:

0.1570 gram substance gave 0.0787 H_2O and 0.4005 CO_2.

	Found.	Calculated, $C_6H_5.CO.CH(CH_2.CH:CH_2).CO_2H.$
C =	69.57 per cent.	70.58 per cent.
H =	5.57	5.78
O =	24.86	23.53

The acid always seems to contain traces of benzoic acid, which spoil the analytical numbers and melting point. It melted at 122–125°, and on further heating either alone or with dilute sulphuric acid, gave off carbonic anhydride and an oil, probably allylacetophenone. I hope later on, if possible, to find some other more suitable means of saponifying diethyl- and allyl-benzoylacetic ethers, and of thus obtaining the acids in a purer state.

Decomposition-products of Allylbenzoylacetic Ether.

The best proof of the formation of allylbenzoylacetic ether in the foregoing experiments was the study of its decomposition-products. In order to examine these, 10 grams of crude allylbenzoylacetic ether were heated for two or three hours with dilute alcoholic potash on a water-bath, by which means it was completely decomposed. After distilling off the alcohol, the residue was diluted with water, and in order to remove the neutral oils from the solution of the potassium salts, it was several times extracted with ether. The ethereal solution, after drying over calcium chloride and distilling off the ether, deposited 5 grams of a dark-brown oil, which was then fractioned.

The principal quantity distilled over between 230° and 240°, and gave on oft-repeated fractionation, an oil boiling constantly at 235–238° (at 710 mm. pressure), which on analysis gave numbers agreeing with those required for allylacetophenone.

0.1248 gram substance gave 0.0852 gram H_2O and 0.3757 CO_2.

	Theory,
Found.	$C_6H_5.CO.CH_2.CH_2.CH:CH_2.$
C = 82.10 per cent.	82.50 per cent.
H = 7.58	7.50
O = 10.32	10.00

Allylacetophenone is formed by the action of alcoholic potash on allylbenzoylacetic ether according to the following equation:

$$C_6H_5.CO.CH(CH_2.CH:CH_2).CO_2C_2H_5 + 2KOH =$$
$$C_6H_5.CO.CH_2.CH_2.CH:CH_2 + K_2CO_3 + C_2H_5OH.$$
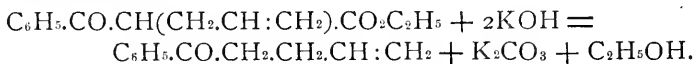
Allylacetophenone is a colorless oil, boiling without decomposition at 235–238° (710 mm.).

It has a curious smell, something like that of camphor, and a burning taste. It is insoluble in water, but dissolves in most of the other solvents. It does not appear to combine with acid sodium sulphite.

The potash salts, which were separated from the allylacetophenone by extraction with ether, were evaporated nearly to dryness on a water-bath, acidulated with dilute sulphuric acid, and distilled in steam. The distillate, which had a strong acid reaction, was filled with drops of an unpleasantly smelling oil, which dissolved easily in a solution of sodium carbonate, and consisted probably of allylacetic acid.

The residue in the retort, on cooling, deposited a quantity of colorless crystals, which were filtered off and recrystallised from water. They then melted at 118–120°, gave with ferric chloride a reddish-brown precipitate, and showed all the properties of benzoic acid. It is therefore probable that part of the allylbenzoylacetic ether had been saponified by the action of the alcoholic potash into allylacetic acid, benzoic acid, and alcohol, according to the following equation :

$$C_6H_5.CO.CH(CH_2.CH : CH_2).CO_2C_2H_5 + 2KOH =$$
$$C_6H_5CO_2K + CH_2 : CH.CH_2.CH_2.CO_2K + C_2H_5OH.$$
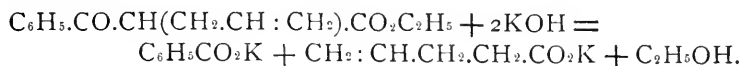
Action of Bromine on Allylacetophenone.

Allylacetophenone being an unsaturated body, it appeared interesting to try the action of bromine on it, in the hope of obtaining a crystalline addition-product. The experiment was carried out in the following way :

Pure allylacetophenone was dissolved in glacial acetic acid, and after weighing the mixture, bromine slowly run in.

The color of the bromine disappeared instantly at first ; after a time, however, much more slowly, without the evolution of hydrobromic acid, the mixture becoming warm, rendering it necessary to cool the mass with water.

As soon as the color of the bromine was permanent, the whole was reweighed, when it was found that 1 mol. of allylacetophenone had taken up two atoms of bromine, according to the equation—

$$C_6H_5.CO.CH_2.CH_2.CH : CH_2 + Br_2 = C_6H_5.CO.CH_2.CH_2.$$
$$CHBr.CH_2Br.$$
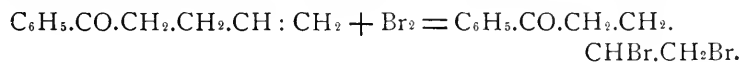
In order to isolate the product, the acid solution was poured into water, allylacetophenone dibromide being precipitated as a heavy oil, which was extracted with ether.

The ethereal solution was then washed once or twice with dilute sodic carbonate to remove any acetic acid, and finally dried over potassic carbonate. After distilling off the ether, a thick colorless oil remained behind, which, after standing over sulphuric acid *in vacuo* for 14 days, did not crystallise.

An analysis of this crude product gave the following numbers :

0.3180 gram substance gave 0.3812 gram $AgBr = 51.01$ per cent. Br. Theory for $C_6H_5.CO.CH_2.CH_2.CHBr.CH_2Br = 50.00$ per cent.

If the solution of allylacetophenone dibromide in glacial acetic acid be further treated with bromine, at the same time warming the mixture on a water-bath, the color of the mixture rapidly disappears, large quantities of hydrobromic acid being given off. In this experiment 4 grams of allylacetophenone dibromide, dissolved in glacial acetic acid, were treated with 1 gram of bromine, the whole being warmed on a water-bath till the reddish color had disappeared.

On pouring the liquid into water, an oil was precipitated which was extracted with ether.

After washing the ethereal solution with sodium carbonate and distilling off the ether, a thick oil remained behind, which, on standing for some days over sulphuric acid in a vacuum, deposited a quantity of crystals. These were roughly separated from the oily products by spreading them out on a porous plate, and finally once or twice recrystallised from dilute alcohol.

The analysis gave the following result:

0.4196 gram of substance gave 0.587 gram AgBr $=$ 59.53 per cent. Br. Theory for $C_{11}H_{11}OBr_3 = 60.15$.

The substance was therefore bromallylacetophenone dibromide.

This body crystallises from dilute alcohol in four-sided prisms which melt at $121-122°$.

It is easily soluble in alcohol, benzene, chloroform, ether, and carbon disulphide. In caustic soda it dissolves with a yellow color.

NOTES OF WORK FROM THE CHEMICAL LABORA-TORY OF THE UNIVERSITY OF VIRGINIA.
No. XIV.[1]

Communicated by W. G. BROWN.

121.—ON A PLATINUM SILICIDE.

BY C. G. MEMMINGER.

In an attempt made to determine the amount of fluorine in a topaz from Stoneham, Maine, by volatilising the fluorine as silicon fluoride, a platinum silicide was formed in the following way.

A platinum crucible containing the powdered topaz was placed in a graphite crucible of such size that between the two crucibles a layer of " Jenning's " calcined magnesia (containing a trace of iron) of 7–10 mm. in thickness was packed, and the top of the graphite crucible carefully luted on with clay.

The crucibles were then placed in a powerful wind furnace fed with " retort carbon," and heated to the highest attainable temperature of the furnace—approximately the fusing point of wrought iron— for about two hours. After cooling, the graphite crucible was opened, and it was found that the platinum crucible had disappeared, and in its place were several metallic buttons mixed with the magnesia which had fritted together, and at the sides had combined with and was firmly attached to the graphite crucible.

The metallic buttons were freed from adhering earthy matters by alternate treatment with strong hydrochloric acid and solution of sodium carbonate.

Thus obtained, the nearly tin-white buttons were slightly attacked, and presented at first glance a frosted appearance; on closer examination it was noticed that on portions of the surface there were radiating straight lines more deeply etched, which were due to an irregular laminated structure.

The silicide is slightly malleable in the cold, but breaks after a few blows, showing a granular fracture, whiter than platinum, which under a pocket lens is seen to consist of the edges of the fractured laminæ intersecting at various angles, in some places giving the impression of an acicular aggregate. Before the blowpipe fusible in small pieces, or on the edges of a fracture. Hardness about 5. Specific gravity 18.97.

It dissolves with difficulty in aqua regia; the surface, during solution, becoming covered with a colorless layer of gelatinous silicic acid which impedes, then finally prevents the action of the solvent, and consequently has to be removed from time to time.

A qualitative analysis showed the presence in small quantity of other metals of the platinum group than platinum.

In the quantitative analysis after solution of the compound in aqua regia, the silica was separated in the usual way, and its purity tested by heating with a solution of pure sodium carbonate. There remained a little quartz sand and a few black scales which appeared to be graphite. The remaining constituents were determined in

the acid solution, but no attempt was made to separate the metals of the platinum group.

The analysis gave

				Ratio.
Platinum,	96.49	.4948 ⎫		
Iron,	.78	.014 ⎬ .5178		9.02
Magnesium,	.21	.009 ⎭		
Silicon,	1.61	.0575	.0575	1.00
Quartz,	.51			
Undetermined,	.32			
	———			
	99.92			

Assuming the iron and magnesium to replace platinum, the formula is Pt_9Si, as above; but if the iron and magnesium are present as impurities the ratio is altered, giving nearly $Pt_{17}Si_2$.

The composition and mode of formation of this silicide varies from that of the few recorded, which may be briefly mentioned.

Berthollet[1] states that Descotils, by the method afterwards used by Boussingault (see below), obtained a button of platinum which was augmented in weight by .03; this augmentation in weight was at the time supposed to be due to carbon, but later experiments indicate that it was probably silicon. The button was very hard, easily broken, brilliant and lamellar in its interior.

Boussingault[2] obtained on heating platinum embedded in charcoal powder in a "creuset brasqué" a fused mass which had a specific gravity of 20.5. On heating strips of platinum embedded in charcoal powder he obtained what he called "platine cementé"; this had a specific gravity of 17.5–18. A silicide prepared by the first method was analysed. In this the amount of silicon was 0.5 per cent. or rather the platinum taken, 1 gram weighed after the experiment 1.005 gram. This silicide possessed essentially the same physical and chemical properties as the silicide which is the subject of this note.

Watts[3] mentions a silicide with 10 per cent. silicon, and one obtained by heating platinum with silicon in excess in the presence of cryolite which had the composition expressed by the formula $PtSi_6$, this is a white compound with gray crystalline fracture.

[1] Annales de Chimie et de Physique **67**, 88, 1808.　　　[2] *Ibid.* **16**, 5 *et seq.*, 1821.
[3] Dictionary of Chemistry **4**, 672.

Boussingault[1] more than fifty years after his first experiments was led to repeat them, and states that the platinum increased in weight from 2.2–5.9 per cent. by its combination with silicon.

A. Colson[2] obtained compounds Pt_2Si and Pt_3Si_2, the latter with a specific gravity of 14.1.

The conditions under which the silicide, which is the subject of this notice, was formed are somewhat similar to those under which P. Schützenberger and A. Colson[3] made their experiments upon platinum silicide previously studied by the latter,[4] and their explanation that the silicon liberated—in this case, by the mutual action of the carbon and silica of the graphite crucible—was diffused in the condition of vapor, either as such or as they prefer, in combination with nitrogen or may be with nitrogen and oxygen, through the magnesia, seems to be more likely than the alternative that the silicon fluoride, driven off from the topaz, was decomposed by the platinum which combined with the silicon and liberated the fluorine. The latter point it is proposed to test experimentally.

122.—ANALYSIS OF A BERYL FROM AMELIA C. H., AMELIA CO., VIRGINIA.

By R. W. Baker.

Among the minerals, some of rare species, found at this locality,[5] are at least four varieties of beryl differing in color : a pale green in large crystals, a darker green in small well defined crystals, a translucent faint purplish or bluish white, and a transparent honey yellow variety. The two latter are frequently found together in the same crystal.

The beryl of which a portion was taken for analysis was a rough crystal, which in part was translucent white, the remainder transparent, varying in color from a wine yellow to a rich honey yellow. This last was separated and analysed. Vitreous to subadamantine lustre. Fracture subconchoidal. Specific gravity 2.702.

A thin section showed under the microscope many fluid inclusions, with and without movable bubbles, but no appearance of alteration or mineral inclusions.

[1] Comptes Rendus **82**, 591, 1876.   [2] *Ibid.* **94**, 26, 1882.   [3] *Ibid.* **94**, 1710, 1882.
[4] *Loc. cit.*   [5] For list of minerals and occurrence see Am. Jour. Sci. III, **25**, May, 1883.

For the separation of the alumina, ferric oxide and glucina the method described by Genth[1] was used. The alumina and glucina after weighing were tested for glucina and alumina, but in neither case was either found to contain the other.

No other alkaline oxide than that of sodium was found, although the others were carefully tested for spectroscopically.

The loss on ignition is put down as water.

The results of the analysis and ratio of the constituents are as follows:

	I.			*a.*	*b.*	
SiO_2	65.24	1.087	1.087	6	7.25	29
Al_2O_3	17.05	.167 ⎫	.181	1	1.21	5
Fe_2O_3	2.20	.014 ⎭				
BeO	12.64	.506 ⎫				
CaO	.57	.010 ⎬	.527	2.91	3.51	14
Na_2O	.68	.011 ⎭				
H_2O	2.70	.150	.150		1.00	4
	101.08					

Considering only the basic oxides and silica, it is seen in *a* that the formula obtained is that commonly received for beryl, $Be_3Al_2Si_6O_{18}$; but if the water is considered essential, as has been proposed by Penfield,[2] the ratio *b* could be written $H_8Be_{14}Al_{10}Si_{29}O_{93}$, which would give the calculated composition II.:

	II.	III.
SiO_2	65.11	65.24
Al_2O_3	19.09	18.45
BeO	13.10	13.14
H_2O	2.70	2.70
	100.00	99.53

This (II) agrees fairly well with the results of the analysis (III), gotten by replacing the ferric oxide, calcium monoxide and sodium oxide in I by the equivalent amounts of alumina and glucina.

The above formula differs considerably from that proposed by Penfield ($H_2Be_5Al_4Si_{11}O_{34}$), and its complexity without further evidence of its correctness is sufficient to prevent its acceptance. At the same time it should not be overlooked that both water and alkalies are probably normal constituents of beryl.

[1] Proceedings Am. Phil. Soc. Phila., **21**, 694. C. N., **51**, 86.
[2] Am. Jour Sci. (3), **28**, 25, 1884:

123.—ANALYSIS OF ALLANITE FROM NELSON CO., VIRGINIA.

By C. G. Memminger.

The locality at which this allanite was discovered is about three miles east of Lowesville, Nelson Co., Va. It is found in a vein at a depth of four to five feet from the surface of the ground, and, as far as it has been examined, the allanite is embedded in detached masses in the lower portion of or just below a "clay" formed by its weathering.

The masses of allanite are rounded, covered with a thin yellowish-white coating. On a surface of fracture the color is pitch black. Resinous lustre. Opaque. Uneven fracture with traces of cleavage. Streak greenish gray. Hardness 6. Specific gravity 3.59. Fuses before the blowpipe with intumescence. Easily decomposed by hydrochloric acid, with separation of gelatinous silica.

It gave on analysis:

SiO_2	30.04	.500	.500	1.97	6
SnO_2	.17	.001			
Al_2O_3	16.10	.158			
Ce_2O_3	11.61	.035			
Di_2O_3	5.39	.016	.254	1.00	3
La_2O_3	4.11	.013			
Fe_2O_3	5.06	.032			
FeO	9.89	.137			
MnO	tr.				
CaO	13.02	.233	.402	1.58	4.8
MgO	1.11	.028			
Na_2O	.28	.004			
K_2O	.02				
H_2O	2.56	.142	.142	.56	1.68
	99.36				

In calculating the ratios the atomic weights of cerium, didymium and lanthanum given by Meyer and Seubert were used, but the probability that the didymia was a mixture was not considered. The molecular ratio for the basic oxides and silica is greater than that now adopted for epidote, $RO : R_2O_3 : SiO_2 = 4 : 3 : 6$. Regarding the

water as non-essential, the formula is nearly $R''_5(R_2)_3^{vi}Si_6O_{26}$, or that of epidote in which the H is replaced by a metal, but if the water is essential the formula becomes $R''_5(R_2)_3^{vi}H_4Si_6O_{28}$.   If in this formula and in the formula for epidote the hydrogen, or what amounts to the same, the water, is regarded as acidic, the oxygen ratio is $1:1$.

124.—ON A DECOMPOSITION PRODUCT OF ALLA-NITE, A VARIETY OF KAOLINITE FROM NELSON CO., VIRGINIA.

By E. P. Valentine.

This substance is a product of the weathering of the allanite described in the preceding note.   It is found in masses preserving the form and structure of that mineral: at times containing in the centre of the mass some unaltered allanite.

It is compact earthy.   Breaks up in angular pieces.   Brownish yellow, yellowish red to red in color.   Adheres to the tongue.   Not plastic.   Crumbles readily between the fingers.   Specific gravity in powder 2.606.

On charcoal blackens and becomes magnetic.   With borax gives the reactions for iron.   Heated in a closed tube gives off water having neutral reaction.

Decomposed by hydrochloric acid.   Decomposed and partially dissolved on boiling with sodium hydroxide.

The particles of the crushed mineral under the microscope are transparent, of a wine yellow color.   The powder is homogeneous, and between crossed Nicols shows no color.

The analysis of the air-dried mineral afforded:

				1	2
SiO_2	18.66	.311	.311	I	2
Al_2O_3	23.28	.228			
Fe_2O_3	34.48	.215			
Ce_2O_3	1.30	.004	.459	1.5	3
La_2O_3	3.27	.010			
Di_2O_3	.65	.002			
MgO	.29	.007			
K_2O	.20	.002	.016		
Na_2O	.43	.007			
H_2O	17.16	.953	.953	3.06	6
	99.72				

Giving the formula $(R_2)_3^{vi}H_{12}Si_2O_{19}$ in which, if the water is considered acidic, the ratio of basic oxygen to acidic $9:10$ is nearly the same as that in the allanite from which this mineral is produced, $1:1$. This is a change similar to that which takes place when beryl alters to kaolinite; there, if the water be considered acidic, the kaolinite retains the oxygen ratio of the beryl, $(Al_2H_4Si_2O_9, 1:2)$. So too in this case there is a loss of protoxides with silica, while at the same time nearly all the rarer oxides have disappeared. There is another view which can be taken of its composition. It is kaolinite in which the two groups H_2O are replaced by two groups $(R_2)^{vi}(OH)_6$. Taking the formula for kaolinite $Al_2Si_2O_7 + 2H_2O$, that just found can be written $(R_2)^{vi}Si_2O_7 + 2[(R_2)^{vi}(OH)_6]^i$ where R_2 is Al_2, Fe_2, Ce_2, Di_2 and La_2. For this view can be cited the replacement of the water of halhydration of the crystallised sulphates of the iron group by an alkaline sulphate, *e. g.* $FeSO_4, H_2O + 6H_2O$ and $FeSO_4, (NH_4)_2SO_4 + 6H_2O$.

If this view be accepted, the compound, assuming its homogeneity, cannot be regarded as a species, and yet it differs sufficiently from kaolinite to have that difference indicated, but this in the present state of mineralogical nomenclature can only be done by adding another name to an already very long list in which species and variety have equal prominence.

This substance is only one of the products of the weathering of allanite. Another analysed by J. R. Santos[2] gave:

[1] These empirical formulæ may be written graphically, using Al to represent the pseudo-triads, thus:

Kaolinite

$$O=Si-O-Al<^{OH}_{OH}$$
$$\overset{|}{O} \qquad |$$
$$O=\overset{|}{Si}-O-\overset{|}{Al}<^{OH}_{OH}$$

$$^{HO}_{HO}>Al-O$$
$$^{HO}_{HO}>Al-O>Si-O-Al<^{OH}_{OH}$$
$$^{HO}_{HO}>Al-O \qquad \overset{|}{O} \qquad |$$
$$^{HO}_{HO}> \overset{|}{\ } -O>\overset{|}{Si}-O-Al<^{OH}_{OH}$$
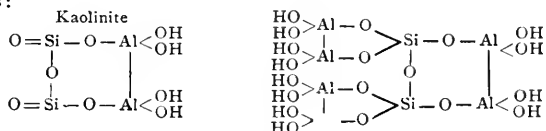
It is not intended by these " ingenious pictorial representations which are sometimes called the structural formulæ of mineral compounds," to convey the idea that this is the actual molecular composition and grouping of the elements, but only to indicate until means are at hand to determine the molecular formulæ of solids, that if it be permitted to assume the valence of elements in the gaseous state for the same elements in solids, that the second of these compounds can be represented as a derivative of the first, the first being a derivative of a metasilicic acid ($H_2Si_2O_5$), and that in both only the ordinarily accepted valences of silicon, aluminum and oxygen are used. Nothing more is intended by these formulæ than to represent a relation, such as is commonly done when sodium acetate is represented as a derivative of acetic acid, or perhaps as sodium acetate is related to silver acetate, or more generally whenever to a solid or liquid is assigned a formula which belongs demonstrably only to the gas.

[2] Chem. News **38**, 95, 1878.

SiO$_2$	21.37	.356	.356	1.04
Al$_2$O$_3$	20.66	.2025 ⎱		
Fe$_2$O$_3$	12.24	.0765 ⎰	.3396	1.00
Ce$_2$O$_3$	21.90	.0606		
BeO	1.95	.08		
H$_2$O	21.37	1.187	1.187	3.5

99.49

The formula found from this analysis R$_2$SiO$_5$ + 3$\frac{1}{2}$H$_2$O is nearly that of miloschite R$_2$SiO$_5$ + 3H$_2$O. It will be seen in this analysis as in the preceding one that the ratio of Al$_2$O$_3$ to R$_2$O$_3$ is nearly 1 : 1.

125.—ANALYSIS OF A FIBROUS BI-SILICATE FROM NELSON CO., VIRGINIA.

By L. G. Patterson.

This mineral occurs interpenetrating the epidotic rocks in the axis of the Blue Ridge at Rockfish Gap Tunnel, Chesapeake and Ohio Railway, Nelson Co., Va.

It is found in the form of wedge-shaped fibrous massive layers, the fibres are parallel, in some specimens a decimetre long and not separable. Olive green to dark green color. Streak grey. Silky lustre. Brittle. Hardness 4. Specific gravity 3.153.

In the forceps fusible to a black glass. In the closed tube darkens, retaining its form. Not entirely decomposed by hydrochloric acid.

A thin section under the microscope appears to be quite fresh and without foreign admixture. It consists of parallel transparent elongated crystals of a light green color.

Its composition was found to be :

SiO$_2$	51.00	.850	.850	15.18
Al$_2$O$_3$	3.05	.029 ⎱		
Fe$_2$O$_3$	4.35	.027 ⎰	.056	1.00
FeO	12.83	.178		
MnO	.60	.008		
CaO	11.20	.200		
MgO	14.24	.356	.757	13.51
K$_2$O	.27	.003		
Na$_2$O	.73	.012		
H$_2$O	2.00	.111	.111	2.00

100.27

The ratio is fairly that of a bi-silicate, but whether pyroxene or amphibole was not determined.

126.—ON A CHLORITE FROM ALBEMARLE CO., VIRGINIA.

By M. Bird.

This mineral is not very abundantly found on Castle Mountain, in the Ragged Mountains about 4 miles south of Batesville, Albemarle Co., Va. It is there looked on as a "kind of soapstone," and it is prized on account of its softness as a material for the bowls of tobacco pipes.

It occurs massive, in small irregularly distributed scales, frequently in curved aggregations, giving the surface of fracture a rough granular appearance. Lustre of scales pearly, of mass glistening. Color olive green. Streak greyish green. Opaque to transparent in thin folia. Folia flexible, not elastic. In powder feels greasy. Tough. Hardness 2.5. Specific gravity 3.05.

In closed tube gives off water and turns black, but the shape of the fragment remains unchanged. Fuses readily to a black glass. On charcoal becomes magnetic. Decomposed by hydrochloric acid with the separation of pulverulent silica.

A thin section under the microscope shows the scales in groups of various forms, fan-shaped, sheaf-like, parallel, lentiform, with a little hydrated ferric oxide between the edges of the groups, otherwise the section appeared homogeneous. Pleochroic.

Analysis afforded :

SiO_2	23.52	.392	.392	1.697	5
Al_2O_3	22.35	.219	.231	1.00	3
Fe_2O_3	1.92	.012			
FeO	28.78	.399			
MnO	.32	.0045	.680	2.944	9
CaO	.39	.0069			
MgO	10.79	.2698			
H_2O	11.28	.626	.626	2.71	8

99.35

Giving the formula $R_9''(R_2)_3^{ri}Si_5O_{28} + 8H_2O$ in which the oxygen ratio of R , $(R_2)^{vi}$, Si, H_2 = 9:9:10:8 or nearly that of corundophilite as given by Dana[1] $1:1:1:\frac{5}{6}$.

In physical characters it appears to resemble more nearly thuringite, in which the oxygen ratio of the basic oxides to that of the silica and water is the same as in the mineral described, *i. e.* 1 : 1.

University of Virginia, *August 18th*, 1885.

[1] A System of Mineralogy, 5th Ed. p. 504.

ON THE DECOMPOSITION OF CINCHONINE BY SODIUM ETHYLATE.

By Arthur Michael.

The first step to an insight into the constitution of the quinine alkaloids was made by Gerhardt,[1] who found that a basic product is formed when quinine and cinchonine are distilled with caustic alkalis, which he called quinoline. The reaction is, however, by no means of so simple a nature as was supposed by the eminent French chemist, for, several years later, it was shown by C. G. Williams that cinchonine yielded, in this process, quite a number of decomposition products. Williams[2] succeeded in isolating from the basic product, besides quinoline, small quantities of pyrrhol bases, several pyridine bases, lepidine and higher boiling homologues belonging to the same series. We are also indebted to Williams[3] for an examination of the higher boiling products, when he obtained from the basic oil boiling above 280°, by a series of fractional distillations and precipitations with platinum chloride, homologues of quinoline up to a compound containing sixteen atoms of carbon. In this paper he conjectured that a base exists among the products of decomposition with the same number of atoms of carbon as are contained in cinchonine. This subject was not exhausted by Williams, as Oechsner[4] has lately shown that reduced quinoline bases are formed, and also that collidine from cinchonine consists of two isomers. Besides basic products, the formation of certain fatty acids has been proven by Lubawin.[5]

In all these investigations the method used was to distil a mixture of the alkaloid and caustic alkali, and examine the products of distillation. It is evident that these compounds may represent but a secondary stage of the reaction, as the alkaloid was exposed to a high temperature and to the energetic action of caustic alkalis. To obviate this, Wischnegradsky and Butlerow[6] have examined the reaction under different conditions, which they unfortunately have not described in their papers.[7] From quinine,

[1] Ann. Chim. et Phys. (III), **7**, 251.   [2] Chem. Gaz., 1855, 301.
[3] Laboratory, 1867, 109.   [4] Ann. Chim. et Phys. (V), **27**.
[5] Berichte 1879, 1254.   [6] *Ibid.* 1878, 1254; 1879, 1480, 2093.
[7] I have not been able to find it described, and have examined all the chemical journals with the exception of the Russian, which were not at my command.

a mixture of $C_{10}H_9NO$ (oxylepidine), ethylpyridine and fatty acids; from cinchonine, quinoline, ethylpyridine and fatty acids were obtained. Basing his speculations on these results, Wischnegradsky[1] suggested that cinchonine contains a reduced pyridine and quinoline group, held together by a propyl radical. These results are certainly in opposition to those of previous investigators; as there is no reason for supposing that the higher boiling bases examined by Williams and Oechsner are formed by distilling quinoline or lepidine with alkalis, and it is a matter of regret that the Russian chemists have not seen fit to publish the method by which they obtained such results.

Another hypothesis on the constitution of cinchonine was suggested by Koenigs,[2] who surmised that it consists of a quinoline and a reduced quinoline group, and that the ethylpyridine formation was due to the action of the alkalis on one of these groups. Somewhat later, judging from the analogous behavior of the carboxyl derivatives of pyridine and cinchene, Koenigs considered it possible that cinchonine contains a reduced pyridine group.

Among the researches on the oxidation of cinchonine may be mentioned, as bearing indirectly on our subject, that of Weidel and Hazura,[3] who have shown that the distillation of the syrupy product obtained in oxidising the alkaloid with potassium permanganate with zinc dust gave ethylpyridine; and that of Comstock and Koenigs,[4] who have isolated from the same oil, by means of bromine, tribromoxylepidine.

In taking up the study of the action of alkalis on the natural alkaloids I have been guided by the following reasons: It seemed to me that the decomposition of the alkaloid should be effected at a moderate temperature, if the primary products of the reaction are to be isolated; and, furthermore, the subsequent action of the alkali should be avoided as much as possible. These conditions are best realised by allowing the alkali and alkaloid to react in solution, by which an intimate contact is insured, and the dilution of the alkali at the same time lessening the likelihood of it acting as a reducing and oxidising agent. My experiments began with heating an alcoholic solution of sodium hydrate and cinchonine in an open vessel connected with reverse cooler. Under these conditions even continued heating for several days caused no apparent

[1] Berichte 1881, 2310.

[2] *Ibid.* 1881, 1852.

[3] Monatsheft für Chemie, 1882, 787.

[4] Berichte 1884, 1990.

decomposition, but when this solution was brought into a closed tube and heated to 100° a decided reaction was noticeable. After making a large number of experiments on the proper proportions and temperature, it was found that heating a solution of six grams of sodium hydrate in 60 cc. of absolute alcohol and six grams of powdered cinchonine[1] to 130–135° for 8 to 10 hours gave the most satisfactory results ; since, when the amount of alcohol was decreased all the cinchonine did not go into solution and eluded decomposition, and heating to a higher temperature, even for a much shorter time, caused the tubes to open under pressure. The greater number of the tubes, when prepared and treated as described, opened without pressure ; some, however, under a slight evolution of an inflammable gas.

The contents of the tubes were brought into a flask connected with a condenser, and the alcohol expelled by heating for a long time in a water-bath ; the thick residue was then added to a large quantity of water, and the mixture extracted several times with ether. After distilling off the ether the residue was treated with steam, as long as the distillate had an odor.

The aqueous distillate was at no time turbid, although in the beginning of the operation it had quite a strong odor, resembling that of quinoline. A quantity of this distillate, obtained from the decomposition product of 250 grams of cinchonine— the basic products weighed over 200 grams—was extracted with ether, dried over $CaCl_2$, and, after evaporating the ether, subjected to a fractional distillation ; but the small amount obtained, about three grams, did not permit a separation of the several products contained in it. About one-half a gram passed over under 65° ; a larger quantity, one and one-half grams, between 100° and 200°, when the thermometer rose rapidly to 250° to 260°, at which temperature about one-half a gram distilled, leaving a small quantity in the flask. The lowest boiling fraction had the odor of pyridine, while the higher boiling portions had a decided quinoline odor. It was thought possible that part of the lower boiling products had gone over with the ether used in extraction ; but on shaking it out with acidulated water, and evaporating the latter to dryness, only a very small residue was left.

As the bases obtained in treating with steam undoubtedly

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[1] The cinchonine used in the first series of experiments contained a small percentage of cinchotine.

contained all the pyrrhol, pyridine and simpler quinoline derivatives formed in decomposing the alkaloid under the above-stated conditions, and hardly more than one per cent. of such products are formed, it is evident that these products represent a secondary reaction—probably an action of the alkali on the primary product. This result is very noticeably different from that obtained in decomposing according to the Gerhardt method, when the greater part of the distillate is composed of such products.

The basic product remaining in the flask after treating with steam was extracted with ether, the extract dried over calcium chloride and the ether evaporated. This left a viscous heavy oil of a reddish color. An attempt to purify this product by distillation at ordinary pressure showed that it decomposed into numerous products ; in fact, it acted exactly like cinchonine does when distilled with alkalis ; and the products obtained were, without doubt, those formed in the Gerhardt reaction. It seemed possible that distillation *in vacuo* would give a more satisfactory result, and 15 grams of crude base were fractioned under about 6 inches pressure at first, but the gaseous products formed soon drove the mercury column down to indicate about 12 inches pressure. The thermometer rose very rapidly to 300°, about 3 grams ; more gradually to 360°, about 6 grams ; and the residue, on cooling, solidified to a hard resinous mass. An attempt to purify these fractions by further distillation *in vacuo* showed that they decomposed into a series of lower boiling products. That, however, these products are not contained in the original product was shown by the fact that after several distillations the greater part of these products passed over very readily with steam. The resinous product remaining in the flask, when distilled under ordinary pressure, gave a series of lower boiling products.[1]

These experiments showed the improbability of purifying the product by distillation, and resort was taken to fractional precipitation with platinum chloride ; a method which, as stated above, yielded good results in separating the higher boiling bases formed in the Gerhardt reaction. For this purpose it was necessary to start with pure cinchonine, and the alkaloid used in the following

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[1] The crude basic product obtained from pure cinchonine appeared to act somewhat different on distillation *in vacuo*. About one-half passed over between 330° and 350°. On redistilling this portion *in vacuo* about one-half passed over under 335°, when about one-third passed over between 335° and 340°. A thermometer place i in the crude base could be heated to 300° without a perceptible quantity of base passing over.

experiments was purified by crystallising the commercial sulphate several times from water, then converting it into the acid sulphate and crystallising this seven times from alcohol, and a final crystallisation of the free base from the same solvent. It was found to be free of cinchotine. The alkaloid was decomposed in the manner described above, and about six grams of the base were dissolved in large excess of hydrochloric acid, filtered from a dark resin which seemed to be formed by the continued treatment of the base with steam, and the solution heated with bone-black, in a flask connected with a cooler, the operation was repeated until another treatment caused no further discoloration. The chlorhydrate was precipitated by adding successively twice 10 cc. of $PtCl_4$ solution (10 per cent.), and three times 15 cc. of the same solution. The first precipitate had a deep reddish-yellow color, the following to the fifth were colored orange, differing from each other but little in intensity, while the fifth had a decidedly deeper tint. All the precipitates of the platinum double salt had the same appearance under the microscope, consisting of round globular plates.

For analysis they were dried at first *in vacuo*, and then at 100° *in vacuo*. They could then be heated to 125° without causing any further loss in weight. It is necessary to dry the double salt *in vacuo* before heating it to 100°, as, when heated at once to that temperature, it melts under the water given off. The precipitates are numbered in the order of their precipitation.

I. 0.4353 gram of precipitate 2 gave 0.5486 gram of CO_2 and 0.1465 gram of H_2O.

II. 0.3186 gram of precipitate 3 gave 0.3972 gram of CO_2 and 0.1175 gram of H_2O.

III. 0.3166 gram of precipitate 4 gave 0.3671 gram of CO_2 and 0.1200 gram of H_2O.

IV. 0.2958 gram of precipitate 5 gave 0.3692 gram of CO_2 and 0.1075 gram of H_2O.

	I.	Found. II.	III.	IV.
C	34.38	34.00	34.23	34.04
H	3.74	4.12	4.22	4.04

A second portion of the base (15 grams), obtained in a subsequent operation, was treated in a like manner, and precipitated by addition of equal weights of platinum chloride. The analyses of the salts, dried at 120°, gave the following results :

I. 0.6480 gram of first precipitate gave 0.1822 gram of Pt.

II. 0.3508 gram of second precipitate gave 0.4394 gram of CO_2 and 0.1310 gram of H_2O.

0.3595 gram of second precipitate gave 0.0984 gram of Pt.

0.4621 gram of second precipitate gave 15.2 cc. of N at 29.5° C. and 763 mm.

III. 0.3138 gram of third precipitate gave 0.3966 gram of CO_2 and 0.1146 gram of H_2O.

0.3529 gram of third precipitate gave 0.0963 gram of Pt.

0.4288 gram of third precipitate gave 0.1183 gram of Pt.

IV. 0.3644 gram of fourth precipitate gave 0.4600 gram of CO_2 and 0.1380 gram of H_2O.

0.3431 gram of fourth precipitate gave 0.0934 gram of Pt.

0.2702 gram of fourth precipitate gave 9.6 cc. of N at 30° C. and 762.3.

V. 0.3683 gram of fifth precipitate gave 0.4563 gram of CO_2 and 0.1270 gram of H_2O.

0.4523 gram of fifth precipitate gave 0.1241 gram of Pt.

	I.	II.	Found. III.	IV.	V.	Theory for $C_{20}H_{28}N_2PtCl_6$.
C		34.13	34.46	34.42	33.90	34.12
H		4.15	4.10	4.20	3.93	3.98
N		4.10		4.41		3.98
Pt	26.56	27.37	27.29 27.59	27.22	27.39	27.69

The consideration of these analytical results leads to the conclusion that the basic product remaining after treating with steam is practically homogeneous ; it containing but a small quantity of foreign bases, which caused the difference between the color of the first precipitate of double platinum salt and the subsequent precipitates, and showed itself in the percentage of platinum contained in the first precipitate.

The base $C_{20}H_{26}N_2$ is a heavy, reddish-yellow, viscous oil, and has, when cold, so great a consistency that it cannot be poured from the vessel containing it ; on heating it becomes mobile. It has a faint odor, resembling slightly that of quinoline ; the odor becomes stronger when the base is heated. Acids dissolve it to form the corresponding salts, which, as far as yet examined, are amorphous. On heating to boiling the base is decomposed into a number of lower boiling bases, probably derivatives of pyridine and quinoline. A solution of the chlorhydrate shows the following reactions :

$SnCl_2$, an amorphous yellowish precipitate.

$HgCl_2$, white amorphous precipitate, but slightly soluble in water.

$K_4Fe(Cn)_6$, pinkish precipitate with the appearance of crystalline structure. Soluble in hot water, but on boiling a precipitate is formed that causes the solution to take a bluish-green fluorescence.

$HgNO_3$, copious yellowish precipitate, which is difficultly soluble in boiling water.

K_2CrO_4, amorphous yellow precipitate, that dissolves in hot water, and separates out on cooling.

$K_3Fe(Cn)_6$, yellowish precipitate, soluble in boiling water.

The symbol $C_{20}H_{26}N_2$ stands in a very simple relation to that of cinchonine, which may be represented by the following equation:

$$C_{19}H_{22}N_2O + C_2H_5ONa = C_{18}H_{21}N_2(C_2H_5) + HCOONa.$$
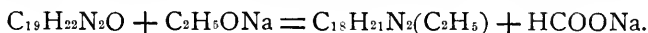
This equation presupposes the existence of an ethyl in the base, which must be derived from the sodium ethylate used in the decomposition, and also the formation of formic acid. Although the examination of the alkaline solution remaining after extracting the base $C_{20}H_{26}N_2$ with ether has not been, from want of time, thoroughly examined, it is probable that it contained formic acid. The alkaline solution was acidulated with sulphuric acid, and treated with steam as long as the distillate showed an acid reaction. The distillate was carefully neutralised with sodium hydrate, and then evaporated to incipient dryness, when it solidified to a white crystalline mass. An aqueous solution of this salt gave on addition of silver nitrate and boiling, a mirror of reduced silver, which is a strong indication of the presence of formic acid.

The experiments described in this note make it very probable that the primary action of alkalis on cinchonine is analogous to that of sodium ethylate, forming the base $C_{18}H_{22}N_2$ and an alkaline formate; and that the bases obtained by previous investigators were due to the decomposition of this base by heat, or by the subsequent action of the alkali. At all events they make the constitution of cinchonine suggested by Wischnegradsky extremely improbable.

If the acid obtained in the above-described decomposition of cinchonine be formic acid, then it would appear that the alkaloid contains a formyl which is easily replaceable; a relation which suggests that cinchonine is an amide of the base $C_{18}H_{22}N_2$ and

formic acid.[1] It seems to me that the above experiments suggest a line of research which will prove very fruitful in the investigation of the natural alkaloids. An experiment with quinine showed that it undergoes a similar decomposition, which makes it probable that all alkaloids yielding quinoline will give analogous results. It is probable that the action of aqueous or dilute alcoholic alkaline solutions on cinchonine will yield the primary product of decomposition; and that a careful investigation of the base described above will throw some light on its constitution. These, and other researches suggested by the above experiments—as well as an examination of the therapeutic properties of the new compounds— will form the subjects of further investigations.

TUFTS COLLEGE, MASS., *July* 6, 1885.

ON SIMULTANEOUS OXIDATION AND REDUCTION BY MEANS OF HYDROCYANIC ACID.

BY ARTHUR MICHAEL AND GEORGE M. PALMER.

It seems to be generally acknowledged that the class of substances playing what is called a catalytic function in chemical reactions undergo some change during the process, although in the end they return to their original form; and the name commonly given implies but an imperfect understanding of this function. It is probable that many of the most important reactions of animal and vegetable life are due to the intercession of such substances. Some of these reactions seem to be dependent on substances capable of decomposing water into its elements, or into hydrogen and hydroxyl; and, when the chemist can command a reagent possessing that property at a low temperature, their imitation in the laboratory may closely follow its discovery.

A substance which is endowed with the property of causing

[1] I was about to make some experiments on the action of sodium ethylate on amides when I received the June number of the Berichte, which contained a paper by R. Seifert (1885, 1355) on the same subject. This chemist shows that sodium ethylate acts on acetanilide and acetamide, forming ethylaniline and ethylamine. It is evident that these reactions are perfectly analogous to that of sodium ethylate on cinchonine.

water to react on certain organic bodies, and apparently at the same time remaining unchanged, is hydrocyanic acid ; although as yet the reactions in which this is known are but few. The first reaction where hydrocyanic acid was used for this purpose was investigated by Strecker,[1] who showed that alloxan, in the presence of ammonia, decomposes hydrocyanic acid into dialuric acid and oxaluramide ; and that not only a small quantity of acid causes a considerable amount of alloxan to decompose, but the decomposition proceeds in the cold. In this paper Strecker made the ingenious surmise that the poisonous properties of hydrocyanic acid may be due to a similar action on the constituents of blood. To the same category of reactions belong the interesting observations of Wallach[2] on the formation of dechloracetic acid, or ether, by the action of HCn on aqueous, or alcoholic, chloralhydrate ; and also that of Böttinger,[3] who obtained lactic and carbonic acids in the action of hydrocyanic and hydrochloric acids on pyruvic acid. The same chemist[4] investigated the behavior of glyoxylic acid towards nascent hydrocyanic acid, and found it is decomposed into glycolic and oxalic acids.

We have undertaken a systematic investigation of the action of hydrocyanic acid, in the presence of water or alcohol, on substances easily susceptible of reduction or oxidation, and hope to ascertain the laws governing its action on such substances. In the present paper will be found the results obtained in the investigation of a number of aromatic compounds.

Action of Alcoholic Hydrocyanic Acid on Benzile.

This reaction has been investigated by Zinin,[5] who obtained an addition-product of one molecule of benzile and two of hydrocyanic acid ; and, lately, the compound has been converted into the amide of an acid.[6] This behavior of benzile towards hydrocyanic acid only takes place when the directions of Zinin are closely followed, as under slightly different conditions quite another result is obtained. We tried, at first, the action of nascent hydrocyanic acid according to the method discovered by Urech. For this purpose 10 grams of benzile and 7.5 grams of pure KCN were mixed, 100 cc. of absolute alcohol added, and

[1] Annalen **113**, 47.   [2] Berichte Annalen **173**, 288.
[3] Annalen **188**, 328.   [4] Berichte, 1877, 1084.
[5] Annalen **34**, 189.   [6] Burton, Berichte, 1883, 2232; also Japp and Miller, *ibid.* 1883, 2418.

the mixture heated until the benzile was dissolved. To the moderately warm solution 10 grams of strong hydrochloric acid (saturated at 8°) were added, drop by drop, and the solution constantly shaken during the operation. The solution, which was reddish brown before adding the acid, became colorless. As much of the alcohol as possible was then expelled, the residue extracted with ether, the ethereal solution separated, and the ether driven off. The residual oil was then shaken with a strong solution of sodium hydrogen sulphite, allowed to stand for some time, and extracted with ether. On evaporation of the ether an oil remained, which was fractionated. The bulk was found to pass over between 205°–208°, and on a second fractionation between 206°–207°. This oil was ethyl benzoate ; as was shown by its physical properties, and by boiling with caustic potash, when it was decomposed into potassium benzoate and ethyl alcohol. From the sulphite solution pearly crystalline plates had separated ; these were the double salt of acid sodium sulphite and benzaldehyde. On adding sufficient sodium carbonate to make the solution alkaline, and boiling, an oil passed over, which boiled at 180°, and was converted into benzoic acid by treating with nitric acid. The amount of ethyl benzoate and benzaldehyde obtained was greater than that of the benzile used.

It is evident from these results that benzile is decomposed by nascent hydrocyanic acid and alcohol quantitatively according to the following equation :

$$C_6H_5COCOC_6H_5 + C_2H_5OH + HCN$$
$$= C_6H_5 - COOC_2H_5 + C_6H_5CHO + HCN.[1]$$

It became of interest to ascertain whether free hydrocyanic acid would cause the decomposition of benzile, and a tube containing twenty grams of benzile, absolute alcohol, and a few cc. of strong hydrocyanic acid was heated at 200° for four hours. The contents of the tube were heated until the alcohol was driven off, water added, then shaken out with ether, and the ethereal solution fractionated. Between 160°–190° benzoic aldehyde passed over—this was proved by forming the addition-product with sodium hydrogen sulphite, and oxidation to benzoic acid—between 190°–210° an oil, which on re-

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[1] Benzile undergoes, according to Jourdan (Berichte, 1883, 658), the same decomposition when exposed to the action of alcohol and potassium cyanide. It does not seem improbable that the decomposition is due to the presence of a small quantity of free hydrocyanic acid.

distilling passed over almost completely from 204°–207°. This fraction consisted of benzoic ether.   Above 210° the thermometer rose rapidly to 250°, when between that temperature and 300° a solid substance distilled.   This substance consisted of rectangular plates, and was shown to be benzoic acid.   It is evident that hydrocyanic acid in a free state possesses equally with the nascent acid the property of decomposing benzile by causing the addition of the elements of alcohol.

Although it seemed very improbable that alcohol alone would decompose benzile, the experiment was made.   It was found that benzile and alcohol could be heated together in a closed tube to 200° without the benzile being in the least decomposed.

Action of Hydrocyanic Acid on Benzoquinone.

According to Levy and Schultz[1] anhydrous hydrocyanic acid is without action on benzoquinone ; this is, however, not the case when the nascent acid is used. Six grams of quinone were dissolved in absolute alcohol, five grams of pure potassium cyanide added—the solution turned dark and warmed perceptibly, indicating that the salt itself reacts on benzoquinone—and eight grams of hydrochloric acid (spec. grav. 1.22) were slowly added to the cold solution. The mixture was allowed to stand for twenty hours, then the alcohol distilled off, water added to the residue and treated with steam.   The liquid remaining after treatment with steam was extracted with ether, which dissolved a black crystalline mass.   This was pressed between bibulous paper and carefully sublimed. By crystallising this product we obtained long hexagonal prisms, melting at 168°–169° and having all the properties of hydrobenzoquinone. The distillate obtained by treating with steam was extracted with ether, and on evaporation of the solvent, a small quantity of an oil remained.   This oil has the odor of guaiacol, and was, perhaps, ethylhydrobenzoquinone.

The reaction has not been sufficiently examined to give a clear insight into its nature, although the reducing power of hydrocyanic acid is very apparent.   It seems not unlikely that an examination of the oil, or a more minute investigation of the products formed than was permitted with the small quantity of quinone used in the above experiment, will show the manner in which the oxygen is employed.   We shall repeat the experiment on a larger scale.

[1] Annalen der Chemie **210,** 143.

Action of Alcoholic Hydrocyanic Acid on Benzoïn.

The study of the action of hydrocyanic acid on benzoïn presented a peculiar interest in view of the formation of the compound from benzoic aldehyde by means of potassium cyanide. If hydrocyanic acid shows in this instance the property of decomposing benzoïn, we should be in possession of a reagent which would enable us to form retrogressively the aldehyde from its carbon-polymer.

Ten grams benzoïn dissolved in absolute alcohol and a small quantity of hydrocyanic acid were heated in a sealed tube at 200° for five hours. The contents of the tube were heated until the alcohol was expelled, water added, and then the mixture extracted with ether. After evaporation of the ether the residue was treated with steam as long as an oil passed over, the distillate shaken out with ether, and the ethereal solution dried and fractionated. The fraction under 200° contained benzoic aldehyde, but a larger portion passed over between 204°–208°, and consisted of benzoic ether.

The formation of benzoic aldehyde by the intercession of alcohol is easily explained, as will be seen from the following equations :

$$C_6H_5CHOHCOC_6H_5 + C_2H_5OH = C_6H_5CH\frac{OC_2H_5}{OH} + C_6H_5CHO$$

$$C_6H_5CH\frac{OC_2H_5}{OH} = C_6H_5CHO + C_2H_5OH.$$
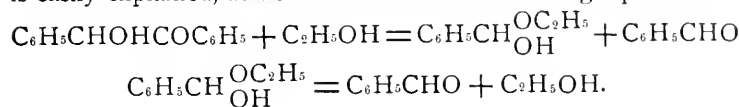
In order to explain the formation of ethyl benzoate it is necessary to assume that it is due to the action of alcoholic hydrocyanic acid on the aldehyde. That benzoic ether is really formed by the action of alcoholic hydrocyanic acid on benzoic aldehyde is proven by the experiment described below. It is certainly an interesting fact that starting with benzoic aldehyde by the use of potassium cyanide it can be converted into its carbon-polymer, while the proper use of the free acid will re-convert the latter compound, at least partially, into the original aldehyde.

Action of Hydrocyanic Acid on Benzoic Aldehyde.

The formation of the nitrile of mandelic acid by the action of hydrocyanic acid on the aldehyde at a moderate temperature indicated that in order that the peculiar reducing and oxidising property of the acid should show itself, it would be necessary to allow the action to take place at a high temperature. We have found that the products of the reaction differ according to whether alcohol or water is used.

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Two grams benzoic aldehyde, some absolute alcohol, and a small quantity of hydrocyanic acid were heated in a sealed tube to 190°–200° for five hours. After evaporating the alcohol, the residual oil was shaken with acid sulphite of sodium and then extracted with ether. The oil, which remained after the ether was expelled, was tested with acid sulphite for unchanged aldehyde, and found to be free of it. It consisted of ethyl benzoate, as was shown by decomposing with caustic potash, and proving the formation of benzoic acid. About three-quarters of a gram of acid was obtained. It seems probably that benzyl alcohol was also formed in this reaction, as is the case when alcoholic potash acts on the aldehyde.[1] The experiment will be repeated on a larger scale, with a view of isolating the other products of the reaction, if such are formed. In the experiment using alcohol instead of water, four grams of the aldehyde, water and one cc. hydrocyanic acid were heated for five hours at 190°–200°. The insoluble oil was shaken with NaHSO₃, then the mixture with ether, which dissolved in oil, having the smell of stryol.

The action of water on benzoic aldehyde at a high temperature was also examined. Two grams aldehyde and water were heated in a sealed tube to 200° for five hours. On treating the contents of the tube as already described, a small amount of benzoic acid was obtained. The quantity, however, was so small that its formation may have been due to the air contained in the tube.

We have also made several experiments on the action of nascent hydrocyanic acid on warm alcoholic solution of phenanthrene-quinone, and have obtained a product quite different from that obtained by Japp and Miller.[2] The product is, if the reaction has proceeded like the analogous diketone already studied, the ether of the half aldehyde of dephenic acid. We shall return to the subject in another paper.

We believe that these experiments suffice to show that hydrocyanic acid possesses in a most marked degree the property of causing certain organic substances susceptible of oxidation and reduction to assimilate the elements of water or alcohol, thereby undergoing a simultaneous oxidation and reduction; and even make it probable that all such compounds will, under the proper conditions of experiment, undergo a corresponding change. We shall continue our investigation in the line already indicated.

TUFTS COLLEGE, *Sept. 20th*, 1885.

[1] Cannizzaro, Annalen **88**, 129.   [2] Berichte, 1883, 2418.

ON THE ACTION OF ALKYL IODIDES ON AMIDO ACIDS.

By Arthur Michael and John F. Wing.

Although it has been known for some years that the intensity with which alkyl iodides enter into reactions differs, to a certain degree, according to the iodide used, it is only lately that this subject has been systematically investigated. Wislicenus[1] has shown that in their action on sodium acet-acetate the iodides of primary radicles show the greatest, the tertiary the least activity; while in the homologous series the iodides of a lower series seem to have relatively a greater activity than that of a higher. It would seem as if this property would show itself, not only quantitatively but also qualitatively, in some of the reactions of the iodides; as yet, however, hardly any facts are known that tend to indicate it. While engaged in the investigation of the action of methyl iodide on asparagine[2] we made a corresponding experiment with ethyl iodide, and were surprised to find a marked difference in the two reactions. This suggested to us that the amido acids are a class of compounds with properties particularly adapted to the examination of the activity of the alkyl iodides; for, evidently, if the iodides shall show qualitative differences in their action on the same substance, this is most likely to occur when bodies are employed that have but a slight affinity for them. P. Griess[3] has noticed, in fact, a qualitative difference in one instance; for he found that when ethyl iodide is heated with potassium metamidobenzoate the mono and diethyl derivatives are formed, no matter in what proportion the reagents are used, while allyl iodide gave only the disubstitution product when the reagents were taken in molecular proportion.

Action of Methyl Iodide on Potassium Paramidobenzoate.

According to Griess,[4] an excess of methyl iodide acts on potassium metamidobenzoate forming the betaine, a strong base that decomposes on distilling into the isomeric dimethylamidobenzoic methyl ether.

[1] **Annalen 212,** 239.   [2] This Journal **6,** 419.   [3] Berichte, 1872, 1033.   [4] *Ibid.* 1873, 585.

For the purpose of examining its action on the para acid, an excess of caustic potash was added to a solution of the acid in methyl alcohol, and then three times the molecular proportion of methyl iodide. This mixture was allowed to stand for four days, during which time further quantities of alkali were added as the solution became neutral. The liquid was then poured off from the potassium iodide that had separated, and evaporated to dryness on the water-bath. After dissolving in water an excess of acetic acid was added, which precipitated the mono and disubstitution products. The filtrate from this acid was evaporated until the greater part of potassium iodide was precipitated, and the filtrate treated with an excess of hydriodic acid. This gave a precipitate consisting of the iodhydrate and periodide of the betaine. These two substances were separated by crystallising from water, the periodide being insoluble it crystallised out on cooling. It consists of long dark prisms, and melts at 200°. On evaporating the filtrate sufficiently and cooling, the iodhydrate was deposited. It has about the same solubility as potassium iodide.

An iodine estimation of the salt gave the following figures :
0.3045 gram of substance gave 0.2333 gram of AgI.

$$\text{Theory for } C_6H_4 \begin{cases} N(CH_3)_3HI. \\ CO{>}O \end{cases}$$

		Found.
I	41.37	41.40

The salt consists of short, yellowish, rectangular plates, melting at 233°. The addition of platinum chloride to a dilute hydrochloric acid solution of it gave the double platinum salt, which forms large red prisms. A platinum estimation gave as follows :

0.356 gram of substance gave 0.0915 gram of Pt.

$$\text{Theory for } \left(C_6H_4 \frac{N(CH_3)_3H}{CO}{>}O \right)_2 PCl_6.$$

		Found.
Pt	25.6	25.7

To obtain the free betaine an aqueous solution of the salt was treated with an excess of freshly precipitated silver oxide, filtered, and the filtrate evaporated to dryness. The base was then extracted by hot alcohol, from which it was deposited on cooling. It contains water of crystallisation. On analysing, the following results were obtained :

0.2885 gram of substance, air-dried, lost 0.0265 gram of H_2O at 100°.

0.2672 gram of substance, dried at 100°, gave 0.6589 gram of CO_2 and 0.1725 gram of H_2O.

Theory for $C_6H_4{<}{{}^{N(CH_3)_3.}\atop{CO}}{>}O$.

		Found.
C	67.04	67.24
H	7.26	7.17

Theory for $C_6H_4{{}^{N(CH_3)_3}\atop{CO}}{>}O\;H_2O$.

		Found.
H_2O	9.14	9.18

The betaine crystallises from alcohol as colorless plates that melt at about 255°. It is readily soluble in water, and forms salts with organic acids, as acetic acid.

The precipitate obtained by addition of acetic acid was found to consist of almost pure dimethylamidobenzoic acid, and melted, without further crystallisation, at 234°. This substance has been already examined by W. Michler,[1] who obtained the mono and diproducts in the action of methyl iodide on amidobenzoate, using the proportion of one molecule of the first to two of the latter compound. An analysis was made :

0.300 gram of acid gave 0.1935 gram of H_2O and 0.7228 gram of CO_2.

Theory for $C_6H_4{{}^{N(CH_3)_2.}\atop{COOH}}$

		Found.
C	65.40	65.70
H	6.60	7.1

Action of Ethyl Iodide on Potassium Paramidobenzoate.

Two separate portions of the reaction, obtained in somewhat different manner, were accidentally mixed, and worked up together. In one portion ten grams of paramidobenzoic acid dissolved in alcohol was treated with an excess of caustic potash, three times the molecular weight of ethyl iodide, and allowed to stand for four days ; in the second a larger proportion of ethyl iodide and alkali were allowed to act for two weeks on four grams of acids. In each case a further quantity of alkali was added as soon as the solutions became neutral. The mixture was heated until free of alcohol and water added to the residue. It was found not to be completely soluble ; a heavy oil remaining undissolved. The liquid was extracted with ether, which dissolved the oil, and the extract, after drying over $CaCl_2$, fractionated. Between 312°-

[1] Berichte, 1876, 401.

$315°$ the oil passed over without decomposition. An analysis was as follows:

0.3081 gram of oil gave 0.2502 gram of H_2O and 0.7969 gram of CO_2.

	Theory for $C_6H_4\overset{N(C_2H_5)_2}{COOC_2H_5}$.	Found.
C	70.59	70.50
H	8.59	9.02

The ether solidifies in a freezing mixture of salt and ice, and is readily soluble in alcohol and ether, insoluble in water. It dissolves in acids to form the corresponding salts, all of which, including the iodhydrate, are soluble in water. Boiled with alcoholic potash, the alcohol driven off and acetic acid added, it gave a precipitate of diethylamidobenzoic acid. The formation is represented by the equation:

$$C_6H_4\overset{NH_2}{COOK} + 3C_2H_5I + 2KOH = C_6H_4\overset{N(C_2H_5)_2}{COOC_2H_5} + 3KI + 2H_2O.$$
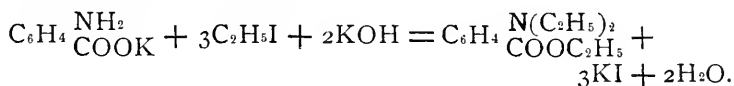
The liquid remaining after extracting with ether was acidulated with acetic acid, and gave a precipitate which consisted solely of diethylamidobenzoic acid. It agreed in its properties with those given by Michler and Gradmann,[1] who obtained it by heating the amidobenzoate with ethyl iodide. For further identification a portion was analysed:

0.1943 gram of substance gave 0.4842 gram of CO_2 and 0.1335 of H_2O.

	Theory for $C_6H_4\overset{N(C_2H_5)_2}{COOH}$.	Found.
C	68.39	67.95
H	7.77	7.83

If the betaine were formed it should have been contained in the filtrate from the diethyl derivative, but the liquid was carefully examined for it without success. It might be thought that the oil contained some, but before distilling it dissolved completely in hydriodic acid, thereby showing its absence.

Action of Allyl Iodide on Potassium Paramidobenzoate.

In this experiment a quantity of acid was dissolved in alcohol, an excess of alkali added, and then three times the molecular

[1] Berichte, 1876, 1912.

proportion of allyl iodide. Like in the preceding experiments, the solution was kept alkaline, and allowed to stand for four days. The residue remaining after evaporation of alcohol dissolved completely in water, and the solution was acidulated with acetic acid. For analysis the precipitate was crystallised several times from alcohol :

0.2546 gram of substance gave 0.671 gram of CO_2 and 0.1509 gram of H_2O.

	Theory for $C_6H_4\frac{N(C_3H_5)_2}{COOH}$	Found.
C	71.89	71.87
H	6.91	6.58

Diallylparamidobenzoic acid crystallises in short, yellowish prisms, melting at 127°. It is insoluble in water, quite readily in hot alcohol. Alkalis and acid dissolve it to form the corresponding salts. This acid is the sole product of the action of allyl iodide on paramidobenzoate. We were unable to find any indication that either the betaine or that the allyl ether of the acid were formed.

By comparing these results it will be seen that each of the alkyl iodides examined in regard to its behavior to paramidobenzoic acid acts in a manner peculiar to itself. While methyl iodide, under the above-described conditions, yielded dimethylamidobenzoic acid and the betaine, the ethyl compound was found to form instead of the betaine its isomer, diethylamidobenzoic ether. A reason for this different behavior may be that the ethyl betaine cannot exist, perhaps undergoes already at ordinary temperature the same decomposition that the methyl betaine does at its boiling point. Finally, it was found that allyl iodide, under the same conditions, yielded neither a betaine nor the corresponding ether, and in this case the sole product is the diallyl derivative.

These results are of interest as showing that the alkyl iodides do not necessarily show the same reactions. We shall endeavor to ascertain whether they are capable of generalisation with other amido acids, and will also examine the action of alkyl iodides of higher series.

Tufts Collfge, Mass., *Sept. 30th,* 1885.

REVIEWS AND REPORTS.

Recent Researches on the Pyridine and Quinoline Bases.

Pyridine Series, $C_nH_{2n-5}N$.—Since the appearance of the last report on these bases in this Journal,[1] additional methods of obtaining pyridine and its derivatives have been discovered. Lieben and Haitinger[2] have treated chelidonic acid with ammonia and distilled the resulting compound with zinc dust. Pyridine was found among the distillation products. Meconic acid was treated in the same way and it also yielded pyridine. By simple transformations, Ost[3] converted meconic acid into picolinic acid. Haitinger[4] has also found that dehydracetic acid can be made to undergo changes similar to those by means of which chelidonic and meconic acids are converted into pyridine. If treated with ammonia, dehydracetic acid is converted into a nitrogenous basic compound, which when distilled with zinc dust yields lutidine.

These reactions are of great interest because they are instances of the simple transformation of non-nitrogenous organic compounds into pyridine derivatives. It is highly probable that the alkaloids and albuminous substances are built up in plants from similar compounds and in a similar way. When we consider that chelidonic and meconic acids occur in plant juices, and that ammonia and nitrates are also present, we can readily understand how reactions of this kind must be of great value in giving an insight into the chemical processes which accompany the assimilation of nitrogen in plant organisms. One of the most characteristic reactions of this kind has been discovered by von Pechmann,[5] who obtained oxynicotinic acid by the action of ammonia upon cumalinic acid. Cumalinic acid is a condensation product obtained by the action of sulphuric acid upon malic acid. When treated with ammonia, water is eliminated, and oxynicotinic acid formed according to the equation:

$$C_5H_3O_2COOH + NH_3 = H_2O + C_5H_3N{<}^{COOH}_{OH}$$
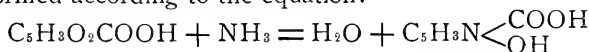
Cumalinic acid.   Oxynicotinic acid.

Chelidonic acid acts in an analogous manner, giving oxypyridine-dicarbonic acid.

$$C_5H_2O_2COOH + NH_3 = H_2O + C_5H_2N{<}^{(COOH)_2}_{OH}$$
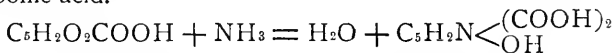
Chelidonic acid.   Oxypyridine-dicarbonic acid.

[1] Vol. **5**, 60.   [2] Berichte der deutschen chem. Gesell. **16**, 1259, 1263.
[3] Journal für praktische Chemie, 1883, **135**, 257.
[4] Berichte der deutschen chem. Gesell. **18**, 452.   [5] *Ibid.* **17**, 2384.

Closely related to these investigations is the work of Behrmann and Hofmann[1] upon the amides of citric acid. These investigators observed that when citramide is treated with sulphuric acid, under certain conditions, it is converted into dioxypyridine-carbonic acid. The latter substance was, by means of phosphorus pentachloride, transformed into dichlorpyridine-carbonic acid, which, on being reduced with hydriodic acid, gave isonicotinic acid.

Beside these reactions of general interest, pyridine derivatives have been obtained by a number of other methods. Waage[2] has obtained a parvoline by the action of heat upon propionic aldehyde ammonia. Hofmann[3] obtained collidine by heating glycol and ammonium chloride to a temperature of 190° in sealed tubes. Ethylidene chloride and ethyl amine treated in the same way also gave collidine. Hofmann has also described a general reaction for the detection of minute quantities of pyridine and its homologues. A few drops of the base to be examined are heated with an equal volume of methyl iodide in a test tube, and pulverised caustic soda or potash added to form a thick paste. If the mixture be gently heated, and pyridine bases are present, a vapor of a highly characteristic but not unpleasant odor will be produced. Ost[4] has found that commercial ammonia frequently contains pyridine, and from one sample of crude ammonia weighing 2½ kilos he obtained several grams of pyridine platinum chloride.

Ladenburg[5] has developed a general method for the synthesis of the homologous pyridine bases. The method is based upon a reaction which Hofmann first used in preparing the homologues of aniline. It consists in making the alkyl addition products of pyridine, and subjecting the resulting compounds to a high temperature in sealed tubes. The addition product is thus changed into the hydriodic acid salt of a substituted pyridine. Ethyl pyridinium iodide was heated in a sealed tube to the temperature of melting lead, and there were formed two isomeric ethyl-pyridines. In the same way two propyl pyridines[6] or collidines were obtained from propylpyridinium iodide.

Piperidine Series, $C_nH_{2n+1}N$.—In the last report[7] it was mentioned that piperidine was regarded as a hexahydropyridine. Our knowledge concerning this subject has been largely extended by the labors of Hofmann and Ladenburg. The intimate relationship existing between these bases has been thoroughly established, and ready means of converting the one into the other have been described. In 1877 Hofmann[8] treated piperidine with bromine and obtained a dibrom-pyridine. This fact led him to suspect that a close connection existed between the two bases. Subsequently Königs[9] confirmed this idea by obtaining pyridine as an oxidation product of piperidine. The transformation was, however,

[1] Berichte der deutschen chem. Gesell. **17**, 2681.   [2] Monatshefte für Chemie **4**, 708.
[3] Berichte der deutschen chem. Gesell. **17**, 1905, 1907, 1909.
[4] Journal für praktische Chemie **136**, 271.
[5] Berichte der deutschen chem. Gesell. **16**, 1410, 2059.   [6] *Ibid.* **17**, 772.
[7] This Journal **5**, 63.   [8] Berichte der deutschen chem. Gesell. **10**, 984.   [9] *Ibid.* **12**, 2341.

exceedingly difficult.   Ordinary oxidising agents gave no results,
and it was only by treating the piperidine with concentrated
sulphuric acid at a temperature of 300° that a very small quantity
of pyridine, hardly sufficient for analysis, was obtained. Hofmann,[1]
in again taking up the subject, expressed the opinion that the
action of bromine upon piperidine consisted, primarily, in the
removal of hydrogen, giving pyridine ; and then, as a secondary
action, the bromine acted upon the pyridine and gave dibrom-
pyridine.   He endeavored, therefore, by working under different
conditions to stop the reaction at the end of the first stage.   For
this purpose piperidine acetate was treated with bromine in the
proportion of one molecule of the former to two of the latter.
Pyridine was found among the reaction products in considerable
quantity.

The comparative ease with which piperidine was thus trans-
formed into pyridine led Hofmann to attempt the reverse change
of pyridine into piperidine.   Königs,[2] previous to this time,
claimed to have obtained some piperidine by reducing pyridine
with tin and hydrochloric acid, but his work left much to be desired,
and Hofmann therefore tried to obtain better results by using
concentrated hydriodic acid.   At temperatures above 300° the
acid acted upon the pyridine, but no piperidine was formed ; the
reducing action was too energetic, and normal pentane and
ammonia were the products.   Ladenburg[3] was the next to take up
the problem, and he began by carefully repeating the experiments
of Königs.   He subjected pyridine to the reducing action of tin and
hydrochloric acid under various conditions, but in no case was
piperidine formed.   After making a great many experiments he
found that by treating an alcoholic solution of pyridine with
metallic sodium, piperidine was readily formed.   The reaction was
found to be almost quantitative, and large quantities of synthetical
piperidine were prepared.   Its properties were then thoroughly
compared with those of the piperidine obtained from the piperine
of pepper, and their identity was established beyond doubt.

Ladenburg[4] then applied this reduction process to the other
pyridine bases.   The picolines, lutidines, and collidines were con-
verted into hexahydro-derivatives which are homologues of piperi-
dine.   In naming the members of this new homologous series he
uses terms which indicate their derivation as well as their relation
to the corresponding members of the pyridine series.   Thus we
have :

Pyridine C_5H_5N	Piperidine $C_5H_{10}NH$
Picoline $C_5H_4(CH_3)N$	Pipecoline $C_5H_9(CH_3)NH$
Lutidine $C_5H_3(CH_3)_2N$	Lupetidine $C_5H_8(CH_3)_2NH$
Collidine $C_8H_{11}N$	Copellidine $C_8H_{17}N$.

Within the last two years the alkaloid coniine has been made
synthetically.   In 1880 Wischnegradsky[5] obtained a pyridine

[1] Berichte der deutschen chem. Gesell. **16,** 588.   [2] *Ibid.* **14,** 1856.   [3] *Ibid.* **17,** 156.
[4] *Ibid.* **18,** 913, 920.   [5] *Ibid.* **18,** 2316.

carbonic acid as one of its oxidation products. After the formula of coniine was found to be $C_8H_{11}N$, it was suspected that it might be a propyl derivative of piperidine. There was no experimental basis for this view, however, until last year, when Hofmann[1] distilled coniine hydrochloride with zinc dust and obtained a base $C_8H_{11}N$ which he called conyrine. Oxidised with potassium permanganate, conyrine was converted into picolinic acid. It therefore seemed highly probable that coniine was an ortho-propyl piperidine. By treating conyrine with concentrated hydriodic acid, coniine was regenerated, which coincided in all its properties with the coniine from hemlock. If now conyrine could be obtained by the introduction of a propyl group into pyridine the synthesis of coniine would be complete. This has been accomplished by Ladenburg,[2] who, by means of his general reaction for making the homologous pyridine bases, succeeded in making an isopropyl pyridine which is identical with conyrine. On reducing this compound with metallic sodium in an alcoholic solution, a hexahydroisopropyl piperidine was obtained, which, in all its properties, physiological as well as physical, is perfectly identical with coniine. As would be expected the synthetical coniine is not optically active.

Quinoline Series, $C_nH_{2n-11}N$.—A general method for the synthesis of quinoline derivatives has been discovered by Friedländer.[3] It consists in bringing together orthoamidobenzoic aldehyde with any aldehyde or ketone in the presence of dilute caustic soda. If acetic aldehyde is used, quinoline is obtained according to the equation :

$$C_6H_4 < \begin{array}{c} C \; \boxed{O}|H \quad \boxed{H_2}|CH \\ \underline{\quad + \quad} \quad | \\ N \; \boxed{H_2} \quad O|CH \end{array} = C_6H_4 < \begin{array}{c} CH - CH \\ | \\ N \; - \; CH \end{array} + 2H_2O.$$
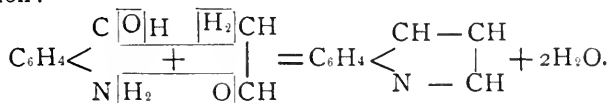
Further study[4] of the reaction showed that it was not limited to acetic aldehyde, but that a whole series of aldehydes and ketones could, by means of orthoamidobenzoic adehyde, be converted into quinoline derivatives. The general reaction is as follows:

$$C_6H_4 < \begin{array}{c} COH \quad CH_2 - B \\ + \; | \\ NH_2 \quad CO \; - A \end{array} = C_6H_4 < \begin{array}{c} CH \\ \diagup \quad \diagdown \\ C - B \\ | \\ C - A \\ \diagdown \quad \diagup \\ N \end{array} + 2H_2O.$$
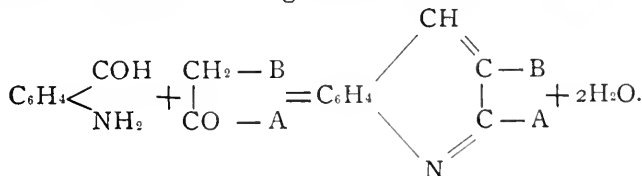
When acetone was used an α-methyl-quinoline or quinaldine was obtained. Acetophenone gave an α-phenyl-quinoline, phenyl-acetic aldehyde gave β-phenyl-quinoline, etc.

[1] Berichte der deutschen chem. Gesell. **17**, 823. [2]*Ibid.* **17**, 1123, 1676. [3]*Ibid.* **15**, 2573. [4]*Ibid.* **16**, 1833.

The synthetical reaction of Doebner and von Miller[1] has also been found to be capable of extensive application in the preparation of substituted quinolines. When ethylene alcohol or paraldehyde is heated with aniline and concentrated hydrochloric acid, a methyl-quinoline or quinaldine is formed. The most probable explanation of the reaction is that crotonic aldehyde is first formed, which then acts upon the aniline and gives an α-methyl-quinoline. By starting with substituted anilines, such as the toluidines, xylidines, etc., substituted quinaldines having the substituting groups in the benzene portion of the compound are obtained. On the other hand, if instead of acetic aldehyde, other aldehydes such as propionic, butyric or valeric aldehyde be taken, then the resulting compounds will be quinaldines having the substituting groups in the pyridine portion of the compound. A large number of such derivatives have been obtained and studied.

The question of the identity or isomerism of the quinoline obtained from cinchonine, and the leucoline from coal-tar or bone-oil, may now be regarded as definitely settled. The only reason for regarding them as isomeric compounds was that the cinchonine-quinoline, when treated with amyl iodide and caustic alkalis, gave the blue coloring matter known as cyanine. In 1879 Hoogewerff and van Dorp,[2] however, obtained the same pyridine dicarbonic acid by oxidising quinoline and leucoline. From their experiments it seemed highly probable that the formation of cyanine was due to the presence of some foreign substance in the quinoline. They[3] have subsequently verified this suspicion by subjecting cinchonine-quinoline to repeated fractional distillation, and then converting it into the chromic acid salt. After a great many recrystallisations the salt was decomposed with caustic soda, and the pure quinoline thus obtained when treated with amyl iodide gave no indication of the formation of cyanine. Cyanine is only produced by the action of amyl iodide upon a mixture of quinoline and lepidine. Quinoline, therefore, from whatsoever source it is obtained, whether from the alkaloids, from bone-oil or coal-tar, or by means of synthetical reactions, is one and the same substance.

Very recently, however, Hoogewerff and van Dorp[4] have found that quinoline in crude bone-oil is accompanied by an isomeric substance. The crude bone-oil quinoline was dissolved in twice its weight of alcohol (95-96 per cent.), and a quantity of concentrated sulphuric acid necessary to convert the base into the acid sulphate salt was added. The solution was allowed to cool, and the acid sulphate salt which separated was decomposed by caustic potash. The basic oil thus obtained was separated by repeated fractional

[1] Berichte der deutschen chem. Gesell. **17**, 1698, 1712.   [2] *Ibid.* **16**, 425.
[3] Recueil des Travaux Chimiques **1**, 1, **2**, 28, 41.   [4] *Ibid.* **4**, 125.

distillation into two parts. One of these boiled from 230° to 236°, and consisted for the most part of quinoline. The other part boiled from 236° to 243°, and contained the new base. This fraction was converted into the sulphate, and recrystallised from alcohol until it fused at a temperature of 200°. The base obtained from the crystalline salt boiled at 236° to 237½° (not corrected); at ordinary temperatures it solidifies in the form of plates which melt at 18° to 23°. Analyses of the compound itself, as well as those of its salts, correspond with the composition expressed by the formula C_9H_7N. It is therefore an isoquinoline.

A consideration of the properties of pyridine and quinoline led Körner in 1870 to suggest that these bases might be analogous to benzene and naphthalene in constitution, that is, their formulae might be represented by closed chains, thus :

```
        H                       H     H
        C                       C     C
      ∧                       ∧         ∧
  HC      CH              HC      C      CH
  |       |               |       |       |
  HC      CH              HC      C      CH
      ∨                       ∨         ∨
        N           .             C     N
    Pyridine.                     H
                              Quinoline.
```
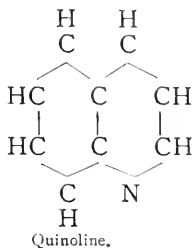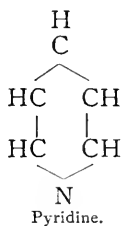
Körner, however, never published this idea. It has been attributed to him by various German writers. Baeyer in his paper on synthetical picolines in Liebig's Annalen for June, 1870, was the first to call attention to it. In the following year Dewar[1] published the same idea. These formulae have been generally accepted. The intimate connection existing between the two bases, their methods of synthesis and transformation into one another, as well as their relation to the benzene hydrocarbons, all seem to be best explained by the assumption of these ring formulæ. The question has recently been raised whether the nitrogen in these compounds is united with three or with two carbon atoms. Riedel[2] has brought forward reasons for believing the former view to be more probable. They are as follows: Graebe and Caro[3] discovered a new base which they called acridine, accompanying crude anthracene. By oxidation acridine was converted into acridinic acid, which by further decomposition was changed into β-quinoline-carbonic acid. Riedel, who had determined the constitution of β-quinoline-carbonic acid, called attention to the fact that the formation of this acid from acridine could only be accounted for by assuming that the latter compound had this formula :

[1] Chemical News, 1871, **23**, 40.   [2] Berichte der deutschen chem. Gesell. **16**, 1609.
[3] Liebig's Annalen der Chemie **158**, 265.

$$\begin{array}{ccccccc}
 & \text{H} & & \text{H} & & \text{H} & \\
 & \text{C} & & \text{C} & & \text{C} & \\
\text{HC} & & \text{C} & & \text{C} & & \text{CH} \\
 | & & | & | & | & & | \\
\text{HC} & & \text{C} & & \text{C} & & \text{CH} \\
 & \text{C} & & \text{N} & & \text{C} & \\
 & \text{H} & & & & \text{H} &
\end{array}$$
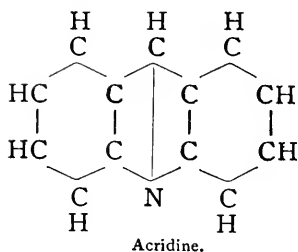
Acridine.

By oxidation we would then obtain acridinic acid :

$$\begin{array}{ccccc}
 & \text{H} & & \text{H} & \\
 & \text{C} & & \text{C} & \\
\text{HC} & & \text{C} & & \text{C}-\text{COOH} \\
 | & & | & | & | \\
\text{HC} & & \text{C} & & \text{C}-\text{COOH} \\
 & \text{C} & & \text{N} & \\
 & \text{H} & & &
\end{array}$$
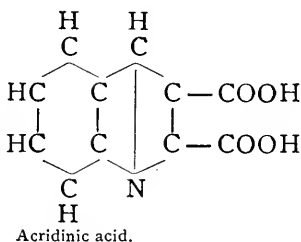
Acridinic acid.

which by heat would be converted into β-quinoline carbonic acid :

$$\begin{array}{ccccc}
 & \text{H} & & \text{H} & \\
 & \text{C} & & \text{C} & \\
\text{HC} & & \text{C} & & \text{C}-\text{COOH} \\
 | & & | & | & | \\
\text{HC} & & \text{C} & & \text{CH} \\
 & \text{C} & & \text{N} & \\
 & \text{H} & & &
\end{array}$$

β-quinoline-carbonic acid.
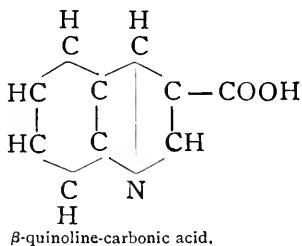
Pyridine and quinoline would then be represented by the following formulae :

$$\begin{array}{ccccc}
 & \text{H} & & \text{H} & \\
 & \text{C} & & \text{C} & \\
\text{HC} & & \text{C} & & \text{CH} \\
 | & & | & | & | \\
\text{HC} & & \text{C} & & \text{CH} \\
 & \text{C} & & \text{N} & \\
 & \text{H} & & &
\end{array}$$

$$\begin{array}{ccc}
 & \text{H} & \\
 & \text{C} & \\
\text{HC} & & \text{CH} \\
 | & & | \\
\text{HC} & & \text{CH} \\
 & \text{N} &
\end{array}$$

Quinoline.
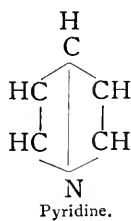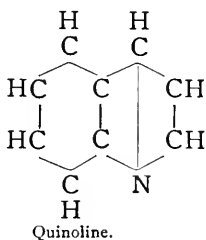
Pyridine.

This view has obtained further support in the recent synthesis of acridine from diphenylamine and formic acid by Bernthsen and

Bender.[1] When diphenylamine and formic acid are brought together in the presence of zinc chloride, a base of the formula $C_{13}H_9N$ having all the properties of acridine is formed. The authors represent the action as follows:
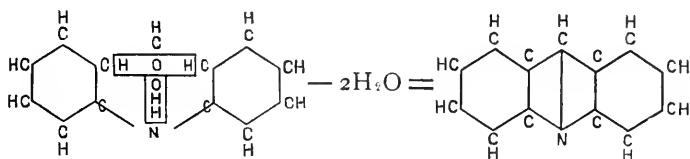
Ladenburg[2] has suggested that acridine may be regarded as related to carbazol, and represents the formula thus

$$\begin{array}{c} C_6H_4—CH \\ | \qquad || \\ C_6H_4—N \end{array}$$

Pyridine would then retain the formula suggested by Körner. To decide between these formulae, Graebe passed tolylphenylamine and benzylideneamine through heated tubes. If Riedel's formula is the correct one, then tolylphenylamine should give acridine according to the equation

$$C_6H_4{<}^{NH—C_6H_5}_{CH_3} = C_6H_4{<}^{N}_{CH}{>}C_6H_4 + 4H.$$
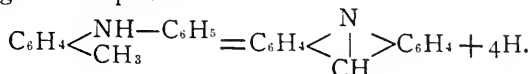
On the other hand, if Ladenburg's formula is correct we would have

$$\begin{array}{cc} C_6H_5—N & C_6H_4—N \\ || & = \quad | \qquad || \qquad + 2H. \\ C_6H_5—CH & C_6H_4—CH \end{array}$$
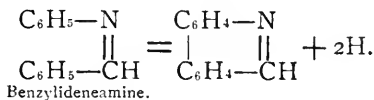
Benzylideneamine.

The experiment showed that the first reaction took place with an abundant yield of acridine, while none could be obtained from the benzylideneamine. All facts known at present are therefore in accordance with the former view of the constitution of acridine.

The question of the relative position of substituting groups with reference to the nitrogen atom in mono-substitution products of pyridine is still an open one. It is highly desirable that the three pyridine-monocarbonic acids, which are so well known, should be classified as ortho, meta and para derivatives. Considerable work has been done in this direction, but not sufficient to warrant drawing definite conclusions. In brief, the problem stands to-day as follows: Skraup,[3] by applying his method for the synthesis of quinoline to *a*- and *β*-naphthylamine, obtained *a*- and *β*-naphtho-quinoline. These compounds, from their method of formation, we are justified in assuming, have the following formulae:

[1] Berichte der deutschen chem. Gesell. **16**, 1803. [2] *Ibid.* **16**, 2061.
[3] Monatshefte für Chemie **4**, 436.
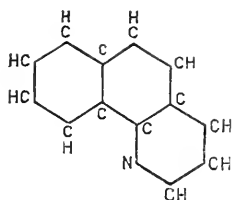
α-naphthoquinoline.
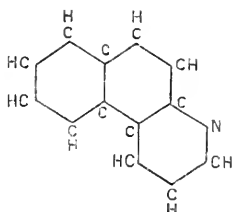
β-naphthoquinoline.

By oxidation of these compounds, acids were formed which on being decomposed gave *a*- and *β*-phenylpyridine respectively.
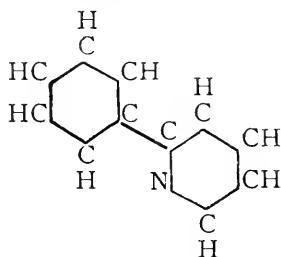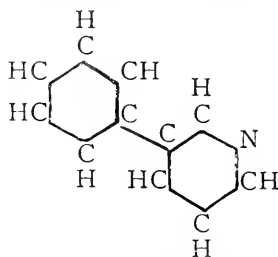
α-phenyl-pyridine.

β-phenyl-pyridine

Further oxidation of these substances converted the former into picolinic acid and the latter into nicotinic acid. Picolinic acid would therefore be an ortho compound, nicotinic acid a meta compound, while the remaining acid, or isonicotinic acid would necessarily be a para derivative. Hoogewerff and van Dorp[1] have, however, raised an objection to this classification, because it was found that there are three pyridine dicarbonic acids which can be converted into isonicotinic acid. If isonicotinic acid is a para compound there can be, theoretically, but two pyridine dicarbonic acids which could be converted into it. The three acids which can be converted into isonicotinic acid are cinchomeronic, lutidinic and Böttinger's pyridine-dicarbonic acids. Skraup, in replying to Hoogewerff and van Dorp's objection to his classification, stated that it would probably be found that Böttinger's dicarbonic acid is identical with cinchomeronic acid. Voigt[2] recently prepared Böttinger's acids for the purpose of making this comparison, and found that these two acids are isomeric compounds of totally different properties, and that there are three pyridine-dicarbonic acids which can be converted into isonicotinic acid. So that the constitution of these three acids is still undetermined, although they are the best known and most thoroughly studied of all pyridine derivatives.

E. H. Keiser.

[1] Berichte der deutschen chem. Gesell. **14,** 646.
[2] Annalen der Chemie **228,** 51.

AMERICAN

CHEMICAL JOURNAL.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

By Wolcott Gibbs, M. D.,

Rumford Professor in Harvard University.

(Continued from Vol. 5, p. 412.)

PHOSPHO-VANADATES.

The existence of a compound of phosphoric and vanadic pent-oxides appears to have been first recognised by Berzelius, who regarded it simply as a phosphate of vanadic oxide and ascribed to it the formula $V_2O_3 . 3P_2O_5$, vanadium being then supposed to have the atomic weight 61.5, so that its highest oxide would have the formula V_2O_3. Berzelius describes the supposed salt as lemon-yellow, crystalline, and slowly soluble in water. By dissolving together sodic phosphate and vanadate, adding nitric acid and evaporating at a gentle heat, he obtained a colorless solution which yielded a lemon-yellow salt in large grains made up of fine crystalline needles. For this compound, which he called phosphate of sodium and vanadic acid, he gave no formula. I shall endeavor to show that phosphoric and vanadic oxides unite in various proportions to form well-defined complex inorganic acids, strictly comparable with those which contain phosphoric and molybdic or tungstic oxides.

Phospho-vanadates are formed when alkaline vanadates are heated in contact with free phosphoric acid; when solutions of an

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[1] Communicated by the Author, from the Proceedings of the American Academy of Arts and Sciences.

alkaline phosphate are digested with vanadic acid or an acid vanadate ; and when alkaline phosphates and vanadates are mixed in presence of a free acid, the conditions being, so far as I have observed, perfectly analogous to those which determine the formation of phospho-tungstates and phospho-molybdates. Phospho-vanadates of the heavy metallic oxides are formed when the divanadates of these oxides are boiled with solutions of alkaline phosphates or with phosphoric acid, and also when the corresponding metallic phosphates are boiled with vanadic acid or acid vanadates. As a rule, the salts are beautifully crystalline, and have a yellow or orange-yellow color, passing in some cases to deep orange-red.

The general characters of the phospho-vanadates are as follows. The alkaline salts have a sulphur-yellow, and in some cases bright yellow color. They are crystalline and often present minute talcose shimmering scales. The relation of these salts to water is especially remarkable. A small quantity of water simply dissolves the phospho-vanadate with a yellow color ; on adding more water, the solution gradually becomes orange, then orange-red, and finally deep red. Phosphoric acid is set free, and one or more new definite salts are formed, in which the proportion of the vanadic to the phosphoric oxide is largely increased. Precisely similar changes occur in the action of water upon arsenio-vanadates. When the deep red solutions are evaporated, the changes of color described occur again in the inverse order, and finally the original yellow salt is again obtained, though not always perfectly free from the higher compound. The facility with which the salts of this series are decomposed by water makes it often difficult to obtain them in a state of absolute purity, and renders the reactions with metallic salts uncertain as characteristics. When alkaline phospho-vanadates are evaporated with nitric acid, the base is in many cases entirely separated, and phospho-vanadic acid remains in solution and may separate in crystals. This separation of fixed base often takes place in presence of an excess of phosphoric acid alone. Solutions of alkaline phospho-vanadates appear to be partially reduced by dust or traces of organic matter with exceptional facility. In such cases the solutions take a more or less distinct greenish color, and phospho-vanadico-vanadates are formed. The solutions of these last salts are not very easily oxidised by bromine or nitric acid, and it is therefore advisable

in preparing phospho-vanadates to avoid as much as possible the presence of reducing agents. Alkaline phospho-vanadates dissolve readily in hot solutions of acid tungstates and molybdates, forming orange or orange-red solutions, which yield in many cases beautiful crystalline phospho-vanadico-molybdates and phospho-vanadico-tungstates.

Analytical Methods.—The method usually adopted for the separation of vanadic and phosphoric oxides by means of ammonic chloride may be successfully applied to the analysis of the phospho-vanadates. A small excess of ammonia is to be added to the solution of the salt, which is then to be heated until it becomes colorless. In this manner we obtain a simple mixture of phosphate and metavanadate. Ammonic chloride is then to be added, and the analysis conducted in the usual manner. This method permits the separate determination of each of the pentoxides and so far offers an advantage. On the other hand, it only applies to salts with alkaline bases. It is far more convenient, and at least equally accurate, to determine the vanadium by titration with hypermanganate under appropriate conditions. The end reaction is usually well defined in a sufficiently dilute solution. The sum of the vanadic and phosphoric oxides may be accurately determined by precipitating the solution of the two pentoxides at a boiling heat by means of mercurous nitrate, adding mercuric oxide until a small but distinct excess is present so as to perfectly neutralise the free acid, and then boiling for a few minutes. Since the ignited mass of oxides retains mercuric oxide with some tenacity, it is best, after burning off the filter with a very free access of air, to add a weighed portion of sodic tungstate and ignite until a constant weight is obtained. When the process is carefully conducted, the fused mass contains all the phosphoric oxide and all the vanadium as pentoxide. Care should be taken to oxidise the whole of the vanadium to pentoxide as more certain. Any small quantity of dioxide present is, however, precipitated when an excess of mercuric oxide is present. This method applies to all salts or compounds containing oxides of phosphorus and vanadium. As regards the details of the determination of vanadium by titration with potassic hypermanganate the following points require attention.

For the reduction of vanadic pentoxide to dioxide, it is best, after adding dilute sulphuric acid, to boil with a solution of sulphurous acid and afterward to evaporate the solution nearly, at

least, to dryness upon a water-bath, so as to insure a perfect reduction and at the same time to expel the last traces of sulphurous oxide. Sulphydric acid gas also readily reduces the vanadic pentoxide in presence of sulphuric acid, but there is almost always a separation of free sulphur in a state of extreme subdivision. This passes readily through the filter, and the results of the titration are not so satisfactory as when sulphurous acid is employed as the reducing agent. The solution of vanadic dioxide should be diluted till the color is pale blue, heated to about 80°–100°, and titrated hot. In the hot solution the disappearance of the hypermanganate takes place instantly, and the end reaction is much more quickly and satisfactorily attained. The actual results are precisely the same as when a cold solution is employed, as the following titrations sufficiently prove.

I. In a cold solution of VO_2 in SO_4H_2 three successive portions of 200 cc. each required 4.62 cc., 4.64 cc., and 4.63 cc. of hypermanganate solution.

II. At 53° C. 200 cc. as before required 4.62.

III. At 62° C. 200 cc. required 4.66 cc. Process rather more rapid.

IV. At 70° C. 200 cc. required 4.66 cc. Process rather more rapid.

V. At 80° C. 200 cc. required 4.65 cc. Color vanished instantly.

VI. At 100° C. 200 cc. required 4.64 cc. Color vanished instantly.

The following analyses will show the effect of reducing by hydric sulphide, as compared with reduction by sulphurous acid. In an acid sodic vanadate:

I. 0.0908 gram gave 0.0406 gram $V_2O_5 = 44.67$ per cent. with H_2S.

II. 0.1381 gram gave 0.0607 gram $V_2O_5 = 43.92$ per cent. with H_2S.

III. 0.1540 gram gave 0.0692 gram $V_2O_5 = 44.90$ per cent. with H_2S.

IV. 0.1625 gram gave 0.0696 gram $V_2O_5 = 42.99$ per cent. with SO_3H_2.

V. 0.1532 gram gave 0.0659 gram $V_2O_5 = 43.01$ per cent. with SO_3H_2.

When hydric sulphide is used as a reducing agent, it often happens that the filtrate on evaporation deposits more sulphur. In titrating with hypermanganate, the final color reaction must be

permanent for ten to fifteen minutes at least. As usual, the amount of hypermanganate required to color an equal volume of water and dilute sulphuric acid must be determined, and the proper correction applied.

In my paper on the vanadio-molybdates I have given another method of determining vanadium based upon the fact that a ferrous salt readily reduces vanadic pentoxide in the presence of free chlorhydric acid. I have since found that this method is not new, but was proposed and tested by Otto Lindemann[1] some years since.

1 : 1 *Ammonic Phospho-vanadate.*—When any ammonic vanadate is dissolved with an excess of ammonic phosphate, and nitric acid is cautiously added in small quantities at a time, a deep orange-red solution is obtained, which on heating becomes colorless, but which on evaporation to a small volume yields beautiful bright yellow granular crystals. These are to be carefully washed with cold water, in which they are not very soluble. The solution has at first a fine yellow color, but on continued dilution with water passes through the changes in color which have already been described. In this salt,

0.5582 gram lost on ignition with WO_4Na_2 0.1017 gram $= 18.22$ per cent.

0.7667 gram lost on ignition with WO_4Na_2 0.1393 gram $= 18.17$ per cent.

0.5329 gram gave 0.0707 gram $(NH_4)_2O = 13.28$ per cent.

0.9753 gram gave 0.4501 gram V_2O_5 with $KMnO_4 = 46.15$ per cent.

0.6883 gram gave 0.3174 gram V_2O_5 with $KMnO_4 = 46.13$ per cent.

0.1073 gram gave 0.0495 gram V_2O_5 with $KMnO_4 = 46.15$ per cent.

The analyses lead to the formula

$$P_2O_5 \cdot V_2O_5 \cdot (NH_4)_2O + Aq,$$
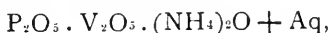
which requires:

		Calc'd.	Mean.
P_2O_5	142	35.99	35.67
V_2O_5	182.6	46.27	46.14
$(NH_4)_2O$	52	13.17	13.28
H_2O	18	4.57	4.91
	394.6	100.00	

[1] Ueber die quantitative Bestimmung des Vanadins. Inaugural Dissertation von Otto Lindemann. Jena, 1879.

I have here assumed that the simplest expression of the results of the analyses represents the molecular weight. It will, I think, appear from the study of other compounds, that it is at least probable that the molecular weight is much higher. The solution of the salt is very easily reduced by dust or traces of organic matter. The solution then contains a greater or less proportion of a phospho-vanadico-vanadate. The solution of the salt has a yellow color and a very strong acid reaction, but this probably depends simply upon the decomposition which sets phosphoric acid free.

1 : 1 *Argentic Phospho-vanadate.*—A quantity of the above-described ammonium salt was dissolved with ammonic phosphate, and argentic nitrate added to the solution in excess. A sulphur-yellow crystalline precipitate was at once formed, which was digested with very dilute nitric acid so as to remove argentic phosphate, and then presented granular yellow crystals but slightly soluble in cold or hot water. The salt is readily decomposed by dilute chlorhydric acid, and then yields a yellow solution which is probably the acid of the series. In the silver salt,

1.4134 gram gave 0.9192 gram $AgCl = 52.59$ per cent. Ag_2O.
1.6267 gram gave 0.7938 gram metallic silver $= 52.41$ per cent. Ag_2O.
1.3696 gram gave 0.2851 gram $V_2O_5 = 20.82$ per cent.
1.0193 gram lost on ignition 0.1067 gram $= 10.47$ per cent.
The analyses lead to the formula

$$P_2O_5 . V_2O_5 . 2Ag_2O + 5Aq,$$
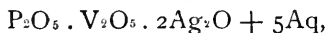
which requires :

		Calc'd.	Found.	
P_2O_5	142	16.19	16.21	
V_2O_5	182.6	20.83	20.82	
$2Ag_2O$	464	52.70	52.59	52.41
$5H_2O$	90	10.28	10.47	
	478.6	100.00		

6 : 4 *Potassic Phospho-vanadate.* — When ammonio-magnesic phosphate, $P_2O_5Mg_2(NH_4)_2$, is boiled with a strong solution of potassic divanadate, the phosphate disappears and is replaced by yellow granular masses, which are but slightly soluble in water. In this salt, after washing with cold water,

0.5401 gram gave 0.3852 gram P_2O_5 and $V_2O_5 = 71.31$ per cent.

0.3790 gram gave 0.1777 gram V_2O_5 with $KMnO_4 = 46.89$ per cent.

0.3790 gram lost on ignition (alone) 0.0619 gram $= 16.31$ per cent.

The analyses lead to the formula

$$4P_2O_5 . 6V_2O_5 . 3K_2O + 21Aq,$$
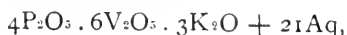
which requires:

		Calc'd.		Found.	
$4P_2O_5$	568	24.41		24.42	
$6V_2O_5$	1098	47.18	71.59	46.89	71.31
$3K_2O$	283	12.16		12.38	
$21H_2O$	378	16.25	28.41	16.31	28.69
	2327	100.00			

No magnesium and no ammonium could be detected in the salt, and it seems at least probable that the salts of the series might be prepared by the same process, other acid vanadates being substituted for the potassic salt employed. A strong solution in cold water gave a brick-red fine granular precipitate with argentic nitrate, and yellow flocky precipitates with mercurous and thallous nitrates. The mercurous precipitate was distinctly seen to contain two different compounds, and it is therefore probable that the potassic salt was decomposed even by a small quantity of cold water.

7 : 6 *Hydric Phospho-vanadate.*—When a solution of phosphoric acid is mixed with a strong solution of sodic divanadate, a yellow uncrystalline mass is formed. This after standing some days becomes distinctly crystalline, and may be washed with cold water until the washings become orange-red. In a preparation of this salt, dried as usual upon woollen paper,

1.2172 gram gave 0.4846 gram $V_2O_5 = 39.81$ per cent.

0.8553 gram gave 0.6487 gram mixed oxides $= 75.84$ per cent. $P_2O_5 + V_2O_5$.

0.6127 gram lost with WO_4Na_2 0.1470 gram $= 24.00$ per cent. water.

The analyses show that the compound analysed contained no soda, and that it is a 7 : 6 phospho-vanadic acid, the formula of which may be written

$$7P_2O_5 . 6V_2O_5 . 3H_2O + 34Aq.$$
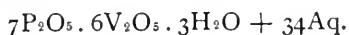
The formula requires:

		Calc'd.		Found.	
$7P_2O_5$	994	39.76 ⎫	75.83	39.81 ⎫	75.84
$6V_2O_5$	1096	36.07 ⎭		36.03 ⎭	
$37H_2O$	666	24.17		24.00	
	2756	100.00			

The sum of the phosphoric and vanadic oxides found by difference is 76.00. After all saline matters are washed out, the acid dissolves readily in water, and gives an orange solution, which changes color on dilution in the manner already explained. I shall, after describing the phospho-vanadico-vanadates and arsenio-vanadico-vanadates, return to this and the preceding compounds.

20 : 1 *Phospho-vanadic Acid.*—When the solution of phosphoric acid is mixed with one of ammonic metavanadate, the liquid becomes orange, but after heating for a time upon a water-bath lemon-yellow, and then deposits a large quantity of a lemon-yellow crystalline salt. More of this salt is deposited on evaporating the mother liquor, and again after partially neutralising with ammonia. The yellow salt may be drained with the filter-pump and then washed with a small quantity of cold water. The salt presents fine yellow crystals, which dissolve in a small quantity of hot water. The liquid is at first yellow, but on adding more hot water, and especially on heating, it becomes orange ; with more water, orange-red, and finally deep garnet-red with a very strong acid reaction. If this solution is evaporated upon a water-bath the changes of color occur in the inverse order ; that is to say, the liquid gradually becomes orange-red, orange, and yellow, and the original salt is finally deposited. The changes of color observed are due to the decomposition of the ammonium salt by water, and the formation of ammonic phosphates and of phospho-vanadates differing in constitution from the original compound and containing a greater proportion of vanadic pentoxide for one molecule of phosphoric oxide. Phosphoric acid is also set free in the reaction. The deep red solution, on standing, deposits beautiful small granular ruby or garnet-red crystals. Of these crystals,

0.3156 gram lost on ignition (alone) 0.0691 gram = 21.89 per cent.

0.3156 gram gave with $KMnO_4$ 0.2377 gram = 75.32 per cent.

The analyses correspond with the formula

$$20V_2O_5.P_2O_5.6H_2O + 53Aq,$$
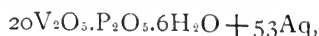
which requires :

		Calculated.	Found.
$20V_2O_5$	3660	75.24	75.32
P_2O_5	142	2.92	2.79
$59H_2O$	1062	21.84	21.89
	4864	100.00	

The phosphoric oxide was determined by the difference. The solution of the acid has a dark red color and a strongly acid reaction. It gives cinnamon-colored flocky precipitates with nitrates of silver and thallium. The silver salt is readily decomposed by potassic chloride in presence of a trace of chlorhydric acid, giving a red solution which deposits beautiful square thin tabular crystals, the red color of which is so deep that they appear black by reflected light. In preparing the salts of this series, it will probably be best to saturate a small proportion of the acid with an alkaline base, and then to add the rest of the acid. For the present the basicity of the acid is undetermined, and the assumption that it contains six molecules of water is merely provisional. It also appears probable that salts of this and similar higher series may be prepared by mixing solutions of alkaline metavanadates with those of alkaline phosphates in definite proportions, and then adding dilute sulphuric acid in small portions at a time, stirring or shaking after each addition of acid. The precise quantity of acid to be added should be calculated beforehand, which may of course be easily done if we assume a definite basicity, as, for instance, that each molecule of salt shall contain three molecules of fixed base.

PHOSPHO-DIVANADATES.

The salts of this series are formed under conditions which have already been pointed out. They have frequently, at least, a fine yellow color, and are decomposed by water with formation of salts of other series.

Phospho-divanadate of Ammonium.—This is the yellow crystalline salt referred to as formed by the action of phosphoric acid upon ammonic metavanadate. The salt dissolves in a small quantity of cold water without apparent decomposition, but the reactions

of the solution are at best rather uncertain. Argentic nitrate gives a fine bright yellow crystalline precipitate. In the ammonium salt,

1.1259 gram lost on ignition 0.2876 gram = 25.54 per cent. NH_3 and H_2O.

1.0600 gram lost on ignition with WO_4Na_2 0.2723 gram = 25.69 per cent.

1.0624 gram gave 0.1676 gram NH_4Cl = 7.67 per cent $(NH_4)_2O$.

1.4112 gram gave 0.7534 gram V_2O_5 = 53.40 per cent.

The analyses lead to the formula

$$P_2O_5.2V_2O_5.(NH_4)_2O.2H_2O + 5Aq,$$
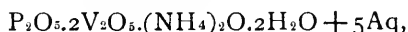
which requires:

		Calculated.	Found.
P_2O_5	142	20.74	20.98 (diff.)
$2V_2O_5$	365	53.28	53.40
$(NH_4)_2O$	52	7.59	7.67
$7H_2O$	126	18.39	17.95
	685	100.00	

The formula given corresponds to the provisional assumption of three molecules of water in the acid.

ARSENIO-VANADATES.

These salts are formed under precisely the same conditions as those which determine the formation of phospho-vanadates. The general characters of the salts are almost precisely similar. Like the phosphorus compounds, they are yellow or orange-yellow and crystalline. They are decomposed by water, and yield deep orange-red salts of new series, in which the proportion of vanadic to phosphoric oxide is largely increased.

Analytical Methods.—Arsenic is most conveniently determined in these salts by reduction with sulphurous acid and precipitation of arsenious sulphide by sulphydric acid. The sulphide is then to be weighed upon an asbestos filter. In the filtrate, which contains the vanadium as dioxide, the vanadic pentoxide may be determined by potassic hypermanganate. Dilute sulphuric acid is to be added in place of chlorhydric acid before precipitation with sulphydric acid. Water cannot be accurately determined in these salts by ignition with sodic tungstate, as a greater or less quantity of arsenic oxide is always volatilised. The best method consists in cautiously

heating the salt over a radiating cup of sheet-iron until a constant weight is obtained.

5 : 8 *Arsenio-vanadic Acid.*—When sodic divanadate and arsenate are dissolved together in boiling water, and nitric acid is added in small portions at a time, a deep orange liquid is obtained which on evaporation to dryness upon a water-bath yields an orange-yellow crystalline mass. This is to be purified by careful washing with cold water, when a beautiful crystalline orange-colored salt remains. The salt is somewhat soluble in cold, and readily in hot water. The solution is very easily reduced by dust or other organic matters, and becomes greenish-orange with formation of a greater or less quantity of an arsenio-vanadico-vanadate. It is then difficult to reoxidise the solution so as to obtain the original compound. On analysis,

$\left\{\begin{array}{l}\text{0.8558 gram gave 0.3374 gram } As_2S_3 = 36.87 \text{ per cent. } As_2O_5. \\ \text{0.8558 gram gave 0.4058 gram } V_2O_5 \text{ with } KMnO_4 = 47.41 \text{ per cent.}\end{array}\right.$

0.8715 gram lost over a radiator 0.1358 gram $= 15.58$ per cent. The analyses correspond to the formula

$$5As_2O_5.8V_2O_5.3H_2O + 24Aq,$$
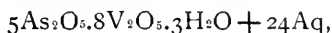
which requires:

		Calculated.		Found.	
$5As_2O_5$	1150	$47.18 \rbrace$	84.31	$47.41 \rbrace$	84.28
$8V_2O_5$	1461	37.13		36.87	
$27H_2O$	486	15.69		15.58	
	3097	100.00		99.86	

The water, as estimated by difference, amounts to 15.72, so that the direct determination is nearly correct, and no fixed base is present. In a second preparation, in which I employed residues containing arsenic and vanadium from the preparation of the arsenio-vanadico-vanadates to be described and oxidised with nitric acid and potassic hypermanganate, I found the ratio of the arsenic to the vanadic oxide to be as 7:6.

$\left\{\begin{array}{l}\text{1.2105 gram gave 0.5825 gram } As_2S_3 = 44.99 \text{ per cent. } As_2O_5. \\ \text{1.2105 gram gave 0.3748 gram } V_2O_5 = 30.97 \text{ per cent.}\end{array}\right.$

The difference here cannot be taken as water, as some manganous oxide was present; but the acid may, like the corresponding phosphorus compound, be regarded as

$$7As_2O_5.6V_2O_5.3H_2O.$$
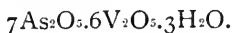
Since the publication of the preliminary notice in which I announced the discovery of this class of compounds,[1] and threw the whole subject open to chemists, a short paper has appeared by F. Fernandez,[2] in which the writer describes an arsenio-vanadate of ammonium, which, except so far as water of crystallisation is concerned, corresponds to the ammonic phospho-vanadate which I have described, so that we now have

$$P_2O_5.V_2O_6.(NH_4)_2O + Aq,$$
$$As_2O_5.V_2O_5.(NH_4)_2O + 11Aq.$$
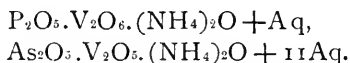
Want of material has prevented a more complete study of the subject on my own part.

PHOSPHO-VANADICO-VANADATES.

The salts of this series are very readily formed by boiling an excess of a mixture of vanadic dioxide and pentoxide with alkaline phosphates, when the mixed oxides dissolve to form red or greenish-red solutions, which on cooling yield in many instances very beautiful crystalline salts. The same result is obtained by fusing the mixture of oxides obtained by igniting ammonic metavanadate with alkaline phosphates; by partially reducing phospho-vanadates, or by adding solutions of vanadic dioxide to solutions of phospho-vanadates. The alkaline phospho-vanadico-vanadates are often very beautiful, and present extremely well-defined crystals. They have usually a green color, which may be so deep as to appear black in large crystals. By oxidation they pass into phospho-vanadates.

Analytical Methods.—These are the same as those described for the analysis of phospho-vanadates. The vanadic dioxide may be determined directly by titration with potassic hypermanganate in dilute solutions containing free sulphuric acid. In another portion of the solutions the vanadic pentoxide is to be reduced with sulphurous acid, and then determined by titration. The whole quantity of oxides may be found by mercurous nitrate and mercuric oxide after completely oxidising the vanadic dioxide with nitric acid.

18 : 1 : 2 *Phospho-vanadico-vanadates of Ammonium.*—When a solution of phospho-vanadate of ammonium is mixed with one of

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[1] This Journal **4**, 577.

[2] Berichte der deutschen chem. Gesellschaft **17**, 1632. July, 1884.

vanadic dioxide in chlorhydric acid, and the liquid is allowed to stand for some time, beautiful deep green prismatic crystals are deposited. These dissolve in hot water to a very deep red solution, and appear to be decomposed exactly in the manner which has been explained in the case of the phospho-vanadates. Of this salt,

0.3647 gram lost on ignition with WO_4Na_2 0.0938 gram $= 25.72$ per cent.

0.5318 gram gave 0.3657 gram V_2O_5 and $P_2O_5 = 68.76$ per cent.

{ 0.4958 gram gave 0.0084 gram VO_2 with $KMnO_4 = 1.68$ per cent.

0.4958 gram gave 0.0083 gram VO_2 with iodine and $CO_3NaH = 1.69$ per cent.

0.4284 gram gave 0.0325 gram $(NH_4)_2O = 7.59$ per cent.

The vanadic dioxide was oxidised with nitric acid before precipitation with mercurous nitrate and mercuric oxide. The resulting percentage is to be corrected accordingly. The analyses correspond fairly well with the formula

$$18V_2O_5 . VO_2 . 2P_2O_5 . 7(NH_4)_2O + 50Aq,$$
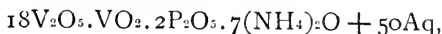
which requires:

		Calculated.	Found.	
$18V_2O_5$	3294	66.88	67.08	
VO_2	83	1.69	1.68	1.74
$2P_2O_5$	284	5.77	5.51	
$7(NH_4)_2O$	364	7.39	7.59	
$50H_2O$	900	18.27	18.13	
	4925	100.00		

The phosphoric oxide is determined by difference only. The compound may also be regarded as a double salt; as, for instance,

$$6V_2O_5 . VO_2 . 3(NH_4)_2O +$$
$$2[6V_2O_5 . P_2O_5 . 2(NH_4)_2O . H_2O] + 48Aq;$$
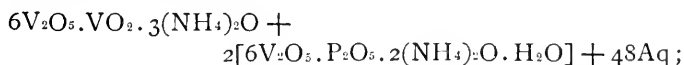
but we have at present no data for deciding the question. The solution in cold water gives brown flocky precipitates with salts of silver and thallium and with mercurous nitrate, none with baric chloride at first, but after a short time the mixture becomes turbid and then deposits distinct orange crystals mixed with a brown flocky matter. The salt is therefore probably decomposed by solution.

4 : 5 : 1 *Phospho-vanadico-vanadate of Sodium.*—A boiling solution of sodic orthophosphate dissolves the mixture of vanadic oxides obtained by igniting ammonic metavanadate, and gives a greenish liquid which on cooling deposits green crystalline scales with a talcose lustre. The same salt is formed by fusing together the mixed oxides and sodic phosphate, but is in this way more difficult to obtain in a state of purity. The compound is insoluble in water, and cannot therefore be purified by recrystallisation. Of this salt,

1.4264 gram lost on ignition 0.3904 gram $= 27.37$ per cent. water.

1.2893 gram gave 0.8136 gram $V_2O_5 + P_2O_5 = 63.10$ per cent.

1.7149 gram gave 0.5815 gram V_2O_5 by titration with $KMnO_4$ $= 33.90$ per cent.

1.4190 gram gave 33.67 per cent. and 33.75 per cent.

—— gram gave 3.11 per cent. VO_2.

The analyses correspond tolerably well with the formula

$$5P_2O_5 . 4V_2O_5 . VO_2 . 4Na_2O + 37Aq,$$
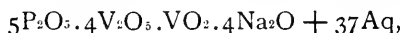
which requires:

		Calculated.	Found.	
$5P_2O_5$	710	29.11	29.15	29 32 (diff.)
$4V_2O_5$	732	30.01	30.66	
VO_2	83	3.40	3.11	
$4Na_2O$	248	10.17	9.74	
$37H_2O$	666	27.31	27.17	
	2439	100.00		

12 : 12 : 6 *Potassic Phospho-vanadico-vanadate.*—When solutions of potassic divanadate and potassic orthophosphate, PO_4K_2H, are heated together, the phosphate being in large excess, a colorless solution is formed. A solution of vanadic dioxide in a large excess of chlorhydric acid then often produces almost immediately a precipitate of black granular crystals. In some cases, however, the black salt is formed only after standing some hours. Under the microscope the black crystals appear to be cubes, though this is rather uncertain. The true color is deep green. The salt is insoluble in water containing other saline bodies; but as soon as the crystals are completely washed, they dissolve readily in hot water with decomposition, a beautiful green salt crystallising from the solution on standing. Of the black crystals,

0.4978 gram lost with WO_4Na_2 0.0716 gram $= 14.38$ H_2O.

0.1622 gram gave with $KMnO_4$ 0.03177 gram $VO_2 = 19.59$ per cent.

0.1201 gram gave with $KMnO_4$ 0.02384 gram $VO_2 = 19.84$ per cent.

0.1383 gram gave with $KMnO_4$ 0.06032 gram $V_2O_5 = 43.62$ per cent.

0.1360 gram gave with $KMnO_4$ 0.05892 gram $V_2O_5 = 43.32$ per cent.

0.5646 gram gave 0.3035 gram $P_2O_7Mg_2 = 34.38$ per cent. P_2O_5.

0.7186 gram gave 0.3876 gram $P_2O_7Mg_2 = 34.49$ per cent. P_2O_5.

The analyses lead to the formula

$$12P_2O_5 . 12VO_2 . 6V_2O_5 . 5K_2O + 40Aq,$$

which requires :

		Calculated.	Found.	
$12P_2O_5$	1704	34.14	34.38	34.49
$12VO_2$	999	20.02	19.84	19.59
$6V_2O_5$	1096	21.96	22.02	21.72
$5K_2O$	472	9.46	9.11	
$40H_2O$	720	14.42	14.38	
	4991	100.00		

The sum of the three oxides $P_2O_5 + VO_2 + V_2O_5 = 76.12$, as calculated from the formula, and 76.02 as found from the mean of all the analyses. The analyses are very difficult, partly because no perfectly satisfactory method of separating phosphoric oxide from the other oxides has yet been found, and partly because in titrating vanadic dioxide by potassic hypermanganate the end reaction varies with the quantity of phosphoric oxide present. It is true that this variation is usually within narrow limits, but it is sometimes sufficient to affect the result by as much as 0.50 per cent.

The beautiful crystalline green salt which is formed when the black salt above described is dissolved in hot water was also analysed.

0.5918 gram gave 0.3771 gram $PtCl_6K_2 = 12.37$ per cent. K_2O.

0.4766 gram lost with WO_4Na_2 0.0718 gram $= 15.06$ per cent.

0.1617 gram gave with $KMnO_4$ 0.03405 gram $VO_2 = 21.06$ per cent.

0.1274 gram gave with $KMnO_4$ 0.02708 gram $VO_2 = 21.26$ per cent.

0.0840 gram gave with $KMnO_4$ 0.01778 gram $VO_2 = 21.16$ per cent.

0.1532 gram gave with $KMnO_4$ 0.0659 gram $V_2O_5 = 43.01$ per cent.

0.1612 gram gave with $KMnO_4$ 0.0689 gram $V_2O_5 = 42.77$ per cent.

0.1625 gram gave with $KMnO_4$ 0.0699 gram $V_2O_5 = 42.99$ per cent.

In the determination of the water by fusion with sodic tungstate, the vanadic dioxide is oxidised to pentoxide. Hence it is necessary to add to the percentage of water found — 15.06 — the percentage of oxygen required to convert 21.16 per cent. (mean) of VO_2 to the equivalent quantity of V_2O_5 or 2.03 per cent. This correction was not applied in the case of the first salt described above, because after a rapid fusion the vanadic dioxide appeared not to have been oxidised. In determining the vanadic pentoxide in these salts the oxide is first reduced to VO_2 by boiling with sulphurous acid and then titrated with hypermanganate. From want of material the phosphoric oxide in the green salt was determined by difference only.

The analyses of the green salt correspond with the formula

$$12P_2O_5 . 14VO_2 . 6V_2O_5 . 7K_2O + 52Aq,$$

which requires:

		Calculated.	Mean.			
$12P_2O_5$	1704	30.63	29.65 (diff.)			
$14VO_2$	1166	20.96	21.16	21.06	21.26	21.16
$6V_2O_5$	1096	19.71	19.73	19.82	19.80	19.58
$7K_2O$	661	11.88	12.37	12.37		
$52H_2O$	936	16.82	17.09	17.09		
	5563	100.00				

In this class of compounds I found it impossible to determine the sum of the acid-forming oxides by precipitating directly with mercurous nitrate and mercuric oxide. The results of many trials varied within very wide limits. Both the black and green salts are oxidised when heated with nitric acid and evaporated to dryness. Yellow crystalline masses remain, which contain phospho-vana-

dates, and which deserve a careful study as furnishing a new and perhaps better mode of forming that class of salts.

14 : 16 : 6 *Ammonic Phospho-vanadico-vanadate.*—When ammonic metavanadate or divanadate is boiled with a solution of ammonic orthophosphate in large excess, a colorless liquid is formed, which gives, with a solution of vanadic dioxide in chlorhydric acid, after a time, beautiful black or rather intensely deep green crystals, exactly resembling those of the potassic salt already described. The crystals dissolve easily in hot water free from saline matter, but do not crystallise readily from the solution. Of this salt, after careful washing and drying only,

0.7744 gram lost with WO_4Na_2 0.1859 gram $= 24.01$ per cent. $NH_3 + H_2O$. The oxygen gained by the vanadic dioxide is 2.14 per cent. and $24.01 + 2.14 = 26.15$ per cent. $NH_3 + H_2O$.

0.5556 gram gave when heated in a combustion tube 0.1451 gram $= 26.11$ per cent. $NH_3 + H_2O$.

0.8969 gram gave with $KMnO_4$ 0.2001 gram $VO_2 = 22.31$ per cent.

0.2018 gram gave with $KMnO_4$ 0.0444 gram $VO_2 = 22.19$ per cent.

0.5626 gram after reduction with SO_3H_2 gave with $KMnO_4$ 0.2427 gram $= 43.13$ per cent. V_2O_5.

0.2494 gram after reduction with SO_3H_2 gave with $KMnO_4$ 0.1067 gram $= 42.76$ per cent. V_2O_5.

0.5325 gram gave 0.0326 gram $(NH_4)_2O = 6.13$ per cent.

0.5053 gram gave 0.0309 gram $(NH_4)_2O = 6.12$ per cent.

The mean of the two determinations of VO_2 is 22.25 per cent., and the equivalent in V_2O_5 24.38 per cent., which, subtracted from 42.76 and 43.13 respectively, gives 18.38 and 18.75 for the percentages of V_2O_5.

The analyses correspond closely with the formula

$$14P_2O_5 \cdot 16VO_2 \cdot 6V_2O_5 \cdot 7(NH_4)_2O + 67Aq,$$

which requires :

		Calc'd.	Found.	
$14P_2O_5$	1988	33.21	33.06 (diff.)	
$16VO_2$	1333	22.26	22.31	22.19
$6V_2O_5$	1096	18.30	18.38	18.75
$7(NH_4)_2O$	364	6.08	6.12	6.13
$67H_2O$	1206	20.15	20.01	
	5987	100.00		

17

A portion of the very dark green salt was boiled with water, and the deep green solution allowed to stand, when much lighter green crystals separated. These were again dissolved and recrystallised. The crystals had a peculiar rusty olive-green surface color. Of this salt,

0.4770 gram gave 0.1013 gram V_2O_5 by $KMnO_4 = 21.21$ per cent., and

0.1014 gram $VO_2 = 21.22$ per cent.

0.4014 gram gave 0.0249 gram $(NH_4)_2O = 6.20$ per cent.

0.3062 gram lost with WO_4Na_2 0.0663 gram $= 21.65$ per cent.

The determination of the sum of the water and ammonia must in this case be corrected for the oxygen required to convert the 21.22 per cent. of vanadic dioxide into vanadic pentoxide, since the ignition was continued with free access of air until the weight of the mass became constant. The correction is of course to be added, so that we have for the total loss $21.65 + 2.03 = 23.68$ per cent.

The analyses correspond tolerably well only with the formula

$$10P_2O_5 . 11VO_2 . 5V_2O_5 . 5(NH_4)_2O + 41Aq,$$
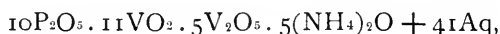
which requires :

		Calculated.	Found.
$10P_2O_5$	1420	33.44 ⎫	33.89 ⎫ (diff.)
$11VO_2$	916	21.57 ⎬ 76.50	21.21 ⎬ 76.32
$5V_2O_5$	913	21.49 ⎭	21.22 ⎭
$5(NH_4)_2O$	260	6.12 ⎫ 23.50	6.20 ⎫ 23.68
$41H_2O$	738	17.38 ⎭	17.48 ⎭
	4247	100.00	

As the number of molecules of vanadic dioxide in this salt is uneven, it will be necessary to double the formula in order to obtain a symmetrical structural scheme.

ARSENIO-VANADICO-VANADATES.

The salts of this series are formed with great ease by mixing solutions of alkaline arsenates and vanadates, and adding a solution of vanadic dioxide in excess of chlorhydric acid. On evaporation large very dark green crystals are deposited in abundance. In preparing arsenio-vanadates it is difficult to avoid a partial reduction of the vanadic pentoxide by dust or other organic matter,

and as a rule solutions are obtained which contain both classes of salts. The arsenio-vanadico-vanadates form a very beautiful and well-defined class of salts.

Analytical Methods.—Vanadic dioxide may be determined directly by titration with hypermanganate after addition of sulphuric acid and appropriate dilution. To determine the arsenic present as arsenic pentoxide, the arsenic is first to be brought into the form of arsenous oxide by means of sulphurous acid after adding a little sulphuric acid to the solution. The arsenic may then be precipitated as sulphide by means of sulphydric acid, and weighed on a Gooch filter. The filrate contains all the vanadium in the form of dioxide, which may then be determined by means of hypermanganate. The relation between the two oxides of vanadium is then easily found. The accurate determination of the water of crystallisation in these salts is difficult. They all lose arsenic oxide when heated with sodic tungstate ; and the only method which can be safely employed consists in heating weighed portions over a radiating cup of sheet-iron until a constant weight is obtained.

12 : 12 : 6 *Ammonium Salt.*—When ammonic metavanadate or divanadate is boiled with a large excess of ammonic arsenate, a colorless solution is formed. On adding a solution of vanadic dioxide in chlorhydric acid, a dark blue precipitate is formed, which dissolves readily in an excess of dilute chlorhydric acid. No precipitate is formed if the solution of the dioxide contains enough free acid. After standing some hours, a very dark green, almost black, crystalline salt is deposited in quantity. This is to be washed with cold water. The crystals exactly resemble those of the black potassic phospho-vanadico-vanadate already described. They are insoluble in saline solutions, and but slightly soluble in cold water. The solution has a greenish-yellow color. It gives a brick-red indistinctly crystalline precipitate with argentic nitrate, and a dull yellow flocky precipitate with mercurous nitrate. This last becomes crystalline on standing. It will serve to prepare other salts of this series by double decomposition with chlorides. The solution of the salt gives no precipitate with cupric sulphate or baric chloride. In this salt,

1.1623 grams gave with $KMnO_4$ 0.2199 gram $VO_2 = 18.91$ per cent.

0.8719 gram gave with $KMnO_4$ 0.3605 gram $V_2O_5 = 41.37$ per cent.

0.9726 gram gave 0.5500 gram $As_2S_3 = 52.87$ per cent.

0.8246 gram gave 0.4646 gram $As_2S_3 = 52.68$ per cent.

1.0209 gram gave 0.0538 gram $(NH_4)_2O = 5.27$ per cent.

The vanadic pentoxide, after deducting the equivalent of the dioxide found, is 20.65 per cent. The water could not be determined either by heating with sodic tungstate or in a combustion tube, as arsenous oxide sublimed in each case. It is therefore estimated by difference.

The analyses agree fairly well with the formula

$$12As_2O_5.12VO_2.6V_2O_5.5(NH_4)_2O + 7Aq,$$

which requires:

		Calculated.	Found.	
$12As_2O_5$	2760	52.65	52.68	52.87
$12VO_2$	1000	19.08	18.91	
$6V_2O_5$	1096	20.91	20.65	
$5(NH_4)_2O$	260	4.96	5.27	
$7H_2O$	126	2.40	2.40	
	5242	100.00		

It will be observed that this salt may be considered as derived from twelve molecules of an arsenio-vanadate by reduction of one-half the vanadic pentoxide to dioxide and loss of seven molecules of ammonic oxide, since we have

$$12[As_2O_5.V_2O_5.(NH_4)O_2] =$$
$$15As_2O_5.12VO_2.6V_2O_5.5(NH_4)_2O + 7(NH_4)_2O + 6O.$$
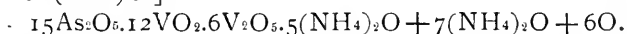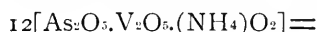
This relation might be made available in the preparation of the salt. Boiling water instantly decomposes this compound, and gives a deep green solution, which on standing deposits crystals of a peculiar deep olive-green color with a tinge of brown. The black salt corresponds exactly in composition to a phosphorus compound above described, except only as regards water of crystallisation :

$$12P_2O_5.12VO_2.6V_2O_5.5(NH_4)_2O + 7Aq.$$

9 : 9 : 8 *Ammonium Salt.*—When boiling water is poured upon the black salt, it instantly becomes deep olive-green upon the surface, and then dissolves to a deep green liquid, which on cooling deposits crystals with a dull olive-green surface color. These may be redissolved and recrystallised a second time. The mother liquor from these crystals has a bright green color, and contains much vanadic acid. In the olive-green salt,

0.4061 gram gave 0.167 gram $(NH_4)_2O = 4.12$ per cent.

{ 0.2871 gram gave 0.1370 gram $As_2S_3 = 44.61$ per cent.

0 2871 gram gave 0.1393 gram V_2O_5 by $KMnO_4 = 48.51$ per cent (complete oxidation).

0.1637 gram gave 0.0259 gram VO_2 by $KMnO_4 = 15.82$ per cent.

The analyses correspond tolerably well with the formula

$$9As_2O_5.9VO_2.8V_2O_5.4(NH_4)_2O + 11Aq,$$
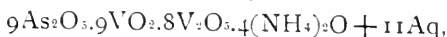
which requires:

		Calculated.		Found.	
$9As_2O_5$	2070	44.17 }	60.17	44.61 }	60.43
$9VO_2$	750	16.00 }		15.82 }	
$8V_2O_5$	1461	31.17		31.17	
$4(NH_4)_2O$	208	4.44		4.12	
$11H_2O$	198	4.22		4.28 (diff.)	
	4687	100.00			

The formula given must be doubled to give a structural scheme in which all the terms will be symmetrically arranged.

It appears at least probable that classes of antimonio-vanadates and antimonio-vanadico-vanadates also exist, but the few experiments which I have been able to make with the small quantity of material at my disposal are not conclusive as to either point, and I hope to be able to return to the subject.

VANADICO-VANADATES.

Salts belonging to this series are formed when solutions of vanadates are mixed with those of vanadic dioxide, and when vanadates undergo partial reduction by the action of any reducing agent. These compounds are often crystalline and well defined. They have, usually at least, a green color.

2 : 4 *Ammonic Vanadico-vanadate.*—When a solution of vanadic dioxide in chlorhydric acid is added to one of ammonic metavanadate, a fine green crystalline salt separates, but slightly soluble in either cold or hot water. The salt analysed was not recrystallised, but merely washed with cold water and dried upon woollen paper. Of this salt,

{ 1.0470 gram gave 0.0159 gram VO_2 by $KMnO_4 = 15.21$ per cent. VO_2.

1.0470 gram gave 0.0701 gram V_2O_5 by $KMnO_4 = 66.98$ per cent. V_2O_5.

0.1470 gram gave 0.0066 gram $(NH_4)_2O = 4.50$ per cent. The analyses lead to the formula

$$4V_2O_5.2VO_2.(NH_4)_2O + 8Aq,$$
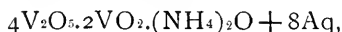
which requires

		Calculated.	Found.
$4V_2O_5$	730.4	66.82	66.98
$2VO_2$	166.6	15.24	15.21
$(NH_4)_2O$	52	4.76	4.50
$8H_2O$	144	13.18	13.31 (diff.)
	1093	100.00	

The following may serve as starting-points for further investigation. When solutions of sodic divanadate and manganous sulphate are mixed and allowed to stand in an open vessel, very dark green well-defined crystals are gradually deposited. There is here, doubtless, reduction from the presence of dust. When a solution of vanadic dioxide in chlorhydric acid is mixed with solutions of the sulphates of zinc, copper, cobalt, or nickel, and of sodic divanadate, dark green crystalline precipitates are formed on standing, which would appear to be vanadico-vanadates, but which, as they are formed in the presence of an excess of a strong acid, may prove to be types of vanadico-vanadic acids. In his valuable paper on the salts formed by vanadic acid, Rammelsberg has described a remarkable compound, which may be regarded as an anhydride of a special form of vanadico-vanadic acid. This compound has the formula

$$V_2O_5 + 2VO_2,$$

and forms black microscopic crystals. Its structural formula may be written:
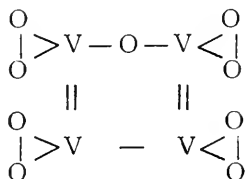
It is easy to see how acids of various types might be derived from such anhydrides by replacing oxygen by an equivalent of hydroxyl. The existence of very well-defined series of phosphoroso-tungstates and phosphoroso-molybdates, and of similar series

of compounds containing As_2O_3 and Sb_2O_3, would naturally lead to the attempt to form similar classes of complex acids containing V_2O_3. Want of material has prevented me from experimenting in this direction, and I must content myself with directing the attention of other chemists to the subject. Vanadic protoxide appears to possess the properties of a base only, but our knowledge of the subject is so imperfect that it may also be well worth while to determine whether there may not be a class of vanadium compounds corresponding to the hypophospho-tungstates and hypophospho-molybdates.

The existence of classes of phospho-vanadates and arsenio-vanadates embraced under the general formula

$$R_2O_3.V_2O_5.nH_2O$$

would seem to imply that of corresponding chlorides, bromides, etc., of corresponding or analogous types,

$$R'Cl_5.RCl_5, \ R'Cl_4.RCl_5, \text{ etc.}$$

Various compounds of this kind have already been observed by chemists, though, so far as I am aware, no attempt has been made to classify them or to assign to them their true position as double chlorides, etc., corresponding to double oxides capable of forming complex acids. Examples of this class are the following:

$SnCl_4 \ + \ PCl_5$	Casselmann.
$SnCl_4 \ + \ POCl_3$	"
$TiCl_4 \ + \ POCl_3$	Weber.
$TiCl_4 \ + \ PCl_5$	Tüttschew.
$SeCl_4 \ + \ SbCl_5$	Weber.
$VOCl_2 + \ PtCl_4$	Brauner.
$Al_2Cl_6 \ + \ 2POCl_3$	Casselmann.
$Fe_2Cl_6 \ + \ 2POCl_3$	"
$SbCl_5 \ + \ PCl_5$	Weber.
$SbCl_5 \ + \ POCl_3$	"

It is at least possible that in these and many similar cases complex or double acids correspond to the double chlorides, and it is probable that the action of such double chlorides upon solutions of acid tungstates and molybdates would produce complex acids containing tungsten or molybdenum and the two acid-forming oxides corresponding to the two united chlorides. I shall

at another time specially consider the compounds of platinous and phosphorous chlorides discovered by Schützenberger.

In my paper upon the vanadium compounds of tungsten and molybdenum I have endeavored to show that many formulas may be reduced to the same types as those of the phospho-tungstates and phospho-molybdates, provided that we assume that a part at least of the vanadic pentoxide is to be regarded as replacing tungstic or molybdic oxide, or that we have the chemical equivalence expressed by the equation

$$m\text{V}_2\text{O}_2 \cdot \text{O}_3 = m\text{WO}_3 = m\text{MoO}_3.$$
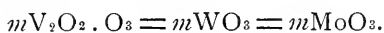
This hypothesis had the advantage of simplifying many formulas materially, but was wholly unsupported by any positive evidence. I have now shown that there exist classes of phospho-vanadates and arsenio-vanadates which do not contain tungstic or molybdic oxide, but which are exactly parallel to phospho-tungstates, vanadio-tungstates, etc., in composition. Thus we have the salt,

$$12\text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot 3\text{BaO} + 45\text{Aq} ;$$

and the acid,

$$20\text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O} + 53\text{Aq} ;$$

corresponding to
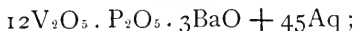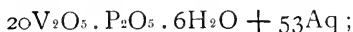
$$12\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3\text{BaO}, \text{ and } 20\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}.$$
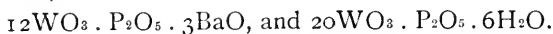
As regards the mode of replacement, however, our views must depend upon the special form of structural formulas which we provisionally adopt. With the view which I have taken of the subject, we may write for a phospho-vanadic acid assumed to have the formula

$$6\text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O},$$
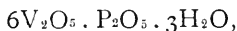
corresponding to the phospho-tungstic acid

$$6\text{WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O},$$

the structural formula,

$$
\begin{array}{c}
\overline{\phantom{\text{VlO}_2 - \text{O} - \text{O} - \text{VlO}_2}} \\
\text{VlO}_2 - \text{O} - \text{O} - \text{VlO}_2 \\
| \qquad\qquad | \\
\text{VlO}_2 - \text{O} - \text{O} - \text{VlO}_2 \\
|| \qquad\qquad || \\
\text{VlO}_2 - \text{O} - \text{O} - \text{VlO}_2 \\
| \qquad\qquad | \\
3(\text{OH}) \equiv \text{PO} \xrule \text{OP} \equiv (\text{HO})_3,
\end{array}
$$

exactly like

$$
\begin{array}{ccc}
\overline{WO_2 - O - O - WO_2} \\
\mid \qquad\qquad \mid \\
WO_2 - O - O - WO_2 \\
\mid\mid \qquad\qquad \mid\mid \\
WO_2 - O - O - WO_2 \\
\mid \qquad\qquad \mid \\
3(OH) \equiv PO \underline{\qquad\qquad} OP \equiv (HO)_3.
\end{array}
$$
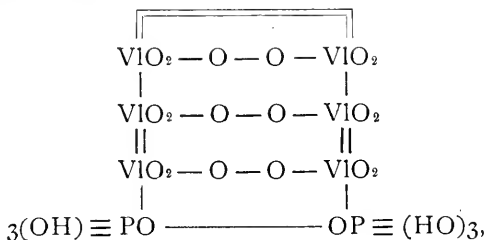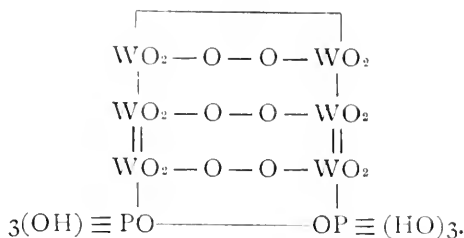
In the formula of the phospho-vanadic acid assumed, I have represented the complex V_2O_2 by VI; and it is easy to see how, structurally, this may be regarded as hexatomic, and as replacing W^{VI} or Mo^{VI}, since we may reasonably suppose that we have

$$
\begin{array}{c}
O - V \equiv \\
\mid \quad \mid \\
O - V \equiv
\end{array}
$$
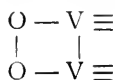
With this view of the subject $(V_2O_2)O_2 = WO_2 = MoO_2$, etc. This mode of formulating compounds containing vanadic pentoxide enables us, as I have shown, to reduce many complex salts to relatively simpler types, and is supported, as we shall presently see, by the formulas of a special class of vanadates exactly corresponding to metatungstates and metamolybdates. On the other hand, in by far the greater number of compounds thus far studied, the complex is to be regarded, I think, as built up of terms of the form RO_2, which may or may not be linked together by one or more atoms of oxygen. In certain cases, therefore, vanadic pentoxide may enter the complex with the structural formula

$$
\begin{array}{cc}
\begin{array}{c}
\mid \\
- V = O_2 \\
\mid \\
O \\
\mid \\
- V = O_2 \\
\mid
\end{array}
&
\text{or as} \quad
\begin{array}{c}
O \mid \qquad \mid O \\
\mid > V - O - V < \mid . \\
O \mid \qquad \mid O
\end{array}
\end{array}
$$
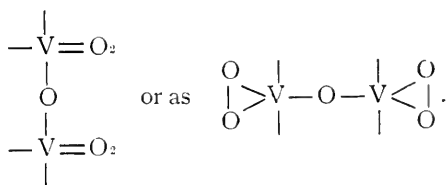
This last view is strongly supported by the frequent presence of vanadic dioxide, two molecules of which may be considered as associated without a link of oxygen, as in the structural formulas

$$
\begin{array}{cc}
\begin{array}{c}
\mid \\
- VO_2 \\
\mid \\
- VO_2 \\
\mid
\end{array}
&
\text{and} \quad
\begin{array}{c}
O \mid \quad \mid O \\
\mid > V - V < \mid . \\
O \mid \quad \mid O
\end{array}
\end{array}
$$
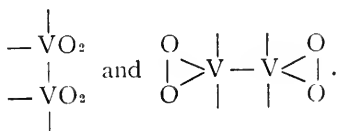
Finally, as I shall also prove, the structural formula must show what particular modification of phosphoric or vanadic oxide or acid is contained in the salt, since we have not merely ortho-phospho-tungstates but pyro-phospho-tungstates, various modifications of metaphospho-tungstates, and corresponding compounds of molybdenum. It is at least probable that the different modifications of vanadic pentoxide or acid enter in a similar manner. These appear to be very numerous, and a wide field is thus opened for research. I shall return to this subject in the purely theoretical portion of my work.

If the view which I have taken as to the composition of the complex acids containing vanadium be correct, we ought to find some additional support for it in the constitution of the salts of vanadic acid. These have been studied by Roscoe, and especially by Norblad[1] and by Rammelsberg,[2] but the results obtained by these chemists have not been systematised. The very numerous vanadates may be arranged, as I find, under seven groups or series. These are here given for the sake of comparison, typical salts actually obtained in each series being marked by the initials of the analysis. The existence of salts corresponding to other general formulæ is a matter of inference only. As will be seen at once, the first series corresponds to the group of metatungstates, if we compare $V_2O_2 . O_3$ with WO_3. Terms 1 and 3 of this series of vanadates have twice the usually given molecular weights.

FIRST SERIES.

Vanadates.		Metatungstates.	
	R_2O . $4V_2O_5$		R_2O . $4WO_3$
R.	$2K_2O$. $6V_2O_5$		$2R_2O$. $6WO_3$
N.	$3Na_2O$. $8V_2O_5 + 24Aq$		$3R_2O$. $8WO_3$
R.	$4Na_2O . 10V_2O_5 + 14Aq$		$4R_2O . 10WO_3$
	$5R_2O$. $12V_2O_5$		$5R_2O . 12WO_3$

SECOND SERIES.

N.	Na_2O . V_2O_5
R.	$2K_2O$. $3V_2O_5$
R.	$3Li_2O$. $5V_2O_5$
	$4R_2O$. $7V_2O_5$

THIRD SERIES.

R.	$K_2O . 2V_2O_5 + 4Aq$
R.	$3Li_2O . 4V_2O_5 + 12Aq$
R.	$5Li_2O . 6V_2O_5 + 30Aq$
	$7R_2O$. $8V_2O_5$

---

[1] Bidrag till kännedomen om Vanadiums Amfidsalter. Upsala Universitäts Årsskrift, 1873.
[2] Sitzungsberichte der Königl. Preuss. Akademie der Wissenschaften, 1883, p. 1.

FOURTH SERIES.

R. $3Li_2O . 2V_2O_5 + 15Aq$
      $4R_2O . 4V_2O_5$
      $5R_2O . 6V_2O_5$
      $6R_2O . 8V_2O_5$

FIFTH SERIES.

R. $2K_2O . V_2O_5 + 3Aq$
      $3R_2O . 3V_2O_5$
      $4R_2O . 5V_2O_5$
      $5R_2O . 7V_2O_5$

SIXTH SERIES.

      $4R_2O . 2V_2O_5$
R. $5K_2O . 4V_2O_5 + 7Aq$
      $6R_2O . 6V_2O_5$
      $7R_2O . 8V_2O_5$

SEVENTH SERIES.

Ro. $3Na_2O . V_2O_5 + 16Aq$
      $4R_2O . 3V_2O_5$
      $5R_2O . 5V_2O_5$
      $6R_2O . 7V_2O_5$
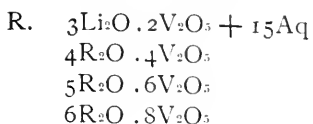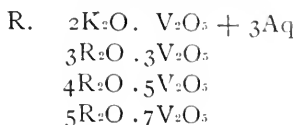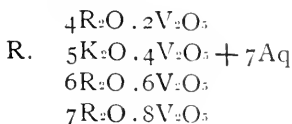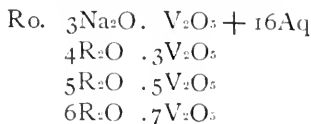
The seven series which I have given embrace, I believe, all known types of vanadates. Each series may be represented by a general formula expressing the relation between the number of molecules of acid and basic oxides. These general formulæ are :

$$I. \quad nR_2O . 2n + 2 . V_2O_5$$
$$III. \quad nR_2O . n + 1 . V_2O_5$$
$$II. \quad nR_2O . 2n - 1 . V_2O_5$$
$$? \quad nR_2O . 2n - 2 . V_2O_5$$
$$V. \quad nR_2O . 2n - 3 . V_2O_5$$
$$IV. \quad nR_2O . 2n - 4 . V_2O_5$$
$$VII. \quad nR_2O . 2n - 5 . V_2O_5$$
$$VI. \quad nR_2O . 2n - 6 . V_2O_5$$
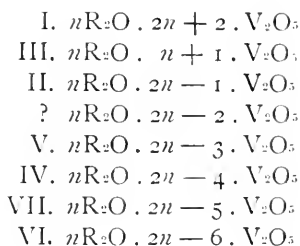
The arrangement here given makes it probable that at least one series remains to be discovered. Fleitmann and Henneberg have described a phosphate having the formula $6Na_2O . 5P_2O_5$. Such a compound would belong to a class of phosphates represented by the general formula--wanting among the vanadates—

$$nR_2O . n - 1 . P_2O_5.$$
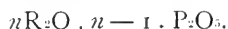
Roscoe long since established the correspondence of the vanadates and phosphates up to a certain limit. Further investigation is required to show how complete the correspondence is. From an examination of the terms in the seven series of vanadates given above, it will appear that various isomeric modifications are probable among vanadates, and that these correspond, in *form* at least, to the various metaphosphates,—mono, di, tri, tetra, and hexa-metaphosphates of Fleitmann and Henneberg. These chemists

have also described a class of phosphates corresponding to the first term of the fourth series of vanadates given above. The sodium salt has the formula

$$3Na_2O . 2P_2O_5 + 18Aq.$$

In the imperfect state of our knowledge, all such coincidences are worthy of attention. Another conclusion may perhaps be safely drawn from the systematic arrangement of the vanadates which I have given. This is that meta, pyro, and ortho-vanadates, and the similar compounds of phosphorus, arsenic, antimony, etc., are not *isolated*, but are terms of more complete series. Thus the fifth series embraces the pyro-vanadates and their homologues, while the ortho-vanadates form the first term of the seventh series. In all the series given except the third, the common difference or homologising term is $R_2O . 2V_2O_5$; in the third series, it is $2R_2O . 2V_2O_5$. In some cases only particular terms may exist to represent an entire series, because the special conditions necessary for the stability of other terms may be absent as regards degree. Taking now into account the analogy which I have shown to exist between $V_2O_2 . O_3$ and WO_3 or MoO_3, we may perhaps extend the above conclusions to the cases of the tungstates, molybdates, chromates, etc. Thus we may regard $K_2O . 2CrO_3$ as the initial term of a series corresponding to the third series of vanadates. If we double the usual formula of potassic terchromate, and write it $2K_2O . 6CrO_3$, we shall have the second term in a series corresponding to that of the metatungstates, the first term being the tetrachromate $K_2O . 4CrO_3$.

As a further support to my view that the metatungstates form a homologous series, I shall here describe two new tungstates obtained since the first part of this work was published.

16 : 3 : 4 *Sodio-ammonic Tungstate.*—I obtained this salt accidentally in attempting to prepare a series of glycero-phospho-tungstates. The thick syrupy liquid obtained by heating pulverised glacial phosphoric acid with glycerine, and allowing the mixture to stand for some days, was neutralised with ammonia and poured into a hot solution of 12 : 5 sodic tungstate. A beautiful white salt, in shimmering talcose scales, separated as the solution cooled. After careful draining, the salt was recrystallised for analysis. The crystals had a fatty lustre, and were quite easily soluble in hot water. No phosphoric acid could be found in the salt by the most careful testing, and no organic matter. In this salt,

2.3796 grams lost on ignition 0.2825 gram $=$ 11.87 per cent.
$\{$ 2.1691 grams lost on ignition 0.2568 gram $=$ 11.84 per cent.
$\{$ 2.1691 grams gave 1.8209 gram $WO_3 =$ 83.94 per cent.
2.0956 grams gave 0.0973 gram $(NH_4)_2O =$ 4.64 per cent.
The analyses correspond to the formula

$$16WO_3 . 3Na_2O . 4(NH_4)_2O + 18Aq,$$
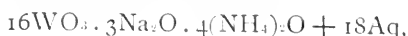
which requires:

		Calculated.	Found.
$16WO_3$	3712	83.79	83.94
$3Na_2O$	186	4.20	4.21 (diff.)
$4(NH_4)_2O$	208	4.69	4.64
$18H_2O$	324	7.32	7.21
	4430	100.00	

This salt is especially interesting because it supplies a new term to the series of metatungstates—the highest as yet obtained.

12 : 1 : 4 *Sodio-ammonic Tungstate.*—This salt was obtained accidentally in an attempt to prepare a series of ethylo-phospho-tungstates. Syrupy phosphoric acid and absolute alcohol were mixed and heated for half an hour to about 80° C., and the mixture allowed to stand twenty-four hours. Ammonia was then added in small quantities at a time until in excess, the liquid being kept cool, the object being to form an ammonic ethylo-phosphate. The solution was then poured into one of 12 : 5 sodic tungstate. After a few minutes an abundant precipitation took place of small shimmering scales, which were drained on the filter-pump, washed with cold water, then dissolved in hot water and filtered. A very small quantity of a very insoluble salt in scales remained undissolved. The filtrate soon gave an abundance of small talcose scales with a fatty lustre.

Of this salt,

1.0293 gram lost on ignition 0.1399 gram $=$ 13.60 per cent.
1.3019 gram lost on ignition 0.1766 gram $=$ 13.57 per cent.
1.0001 gram gave 0.0618 gram $(NH_4)_2O =$ 6.18 per cent.
1.0293 gram gave 0.8689 gram $WO_3 =$ 84.46 per cent.
The analyses correspond to the formula

$$12WO_3 . Na_2O . 4(NH_4)_2O + 14Aq,$$
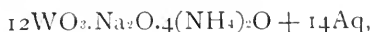
which requires:

		Calculated.	Found.
$12WO_3$	2784	84.22	84.46
Na_2O	62	1.87	1.94 (diff.)
$4(NH_4)_2O$	208	6.29	6.18
$14H_2O$	252	7.62	7.42
	3306	100.00	

No trace of phosphoric acid could be detected in the salt, which is perhaps only interesting as furnishing additional evidence of the existence of a class of meta-tungstates in which the ratio of the tungstic oxide to the oxygen of the base is as 12 : 5. In this, as in the 16-atom salt above described, the presence of an excess of free ammonia explains the absence of phosphoric oxide in the compound formed.

My work on the compounds of vanadium is far less complete and thorough than I could have wished, on account of the relatively very high cost of the material. I indulge the hope that what I have done will be found at least substantially correct, and that the whole subject will soon receive the attention of other chemists, who may have a more abundant supply of vanadium salts at their disposal.

(*To be continued.*)

II.—MARCHAND DE FECAMP'S METHOD FOR THE DETERMINATION OF FAT IN MILK.

By G. C. Caldwell and S. W. Parr.

While one of us was engaged in 1880 in testing this method for the determination of fat in milk, better known by the name which was given to the special instrument used, Marchand's lactobutyro-meter, it was observed that, although the results were in general satisfactory, still there were occasionally differences ranging from 0.2 up to more than 0.4 per cent., between the gravimetric results

and those given by this method.[1]   It was further observed that when bran was contained in the ration of the cows producing the milk examined, the difference between the results given by the two methods was in some cases as great as 0.73 per cent.; when the bran was left out of the ration, fairly correct results were obtained again.   Since then, other similar unsatisfactory results have been obtained under similar conditions, with differences, in the case of a herd of cows having both bran and malt sprouts in their fodder, of over 1 per cent. between the lactobutyrometric and gravimetric methods.   The difference was always a deficiency, and was generally largest with richer milk containing from 4.6 to 4.8 per cent. of fat; but this is not above the limits of the table given by Marchand for reading off the per cent. of fat for the thickness of the ether-fat solution in the lactobutyrometer, nor were the erroneous results always confined to rich milk.   The conclusion seems to be unavoidable that the milk is in some way affected by the feed of the cow so as to hinder the solution, in the normal manner, of the fat of the milk by the ether.

Tollens and Schmidt[2] examined this method very carefully, making some improvements in it, and obtained results nearly always within 0.2 per cent. of the gravimetric results, and usually much closer than this.   The method as described by them was the one followed in the above-mentioned trials, except that a very little acetic acid was first added to the milk, as prescribed by Marchand, but regarded as unnecessary by them; much better results were obtained in this laboratory with it than without it.

Unsatisfactory results have been reported also by others besides ourselves.[3]   Liebermann, while allowing, as most of the other authors referred to also do, that good results are usually obtained, suggests that his poor results may be due to some quality of the milk dependent on the age of the cow; we have tested this suggestion, but could not confirm it.

Vieth,[4] chemist of the Aylesbury Dairy Company (English), has tested the method by comparing the results obtained on 1439 samples of milk with gravimetric results; he concludes that with milk containing from 3.0 to 3.6 per cent. of fat the results are satis-

[1] First Report, Cornell University Experiment Station, 1880, 59.

[2] Journal für Landwirtschaft, 1878, 361 ; 1879, 145.

[3] Thoenor : Repertorium der analytischen Chem. **4**, 100. Skalweit : *Ibid.* **4**, 132. Labesius : Milch Zeitung **13**, 760. Liebermann : Fres. Zeitschrift **23**, 485.

[4] Forschungen auf dem Gebiete der Viehhaltung, 1885, 2d series, 349.

factory, but that with poorer or richer milk they are not ; the results with the former being sometimes as much as 1 per cent. and often 0.5 to 0.6 too high, and with the latter sometimes 0.4 per cent. too low.   But while mentioning the poverty or richness of the milk in fat as one of the conditions affecting the results of its determination by the lactobutyrometer, he acknowledges that other conditions also affect the working of the process, and among these he mentions briefly the feed of the cow.

Others commend the method without qualification.   Dietzsch,[1] chemist of the Anglo-Swiss Condensed Milk Company, states that of from fifty to a hundred determinations of fat made every day in his laboratory by this method, many are controlled by gravimetric methods, and that the results by the two methods always agree within 0.1 per cent.   H. von Peter[2] affirms that the method gives good results, even in unskilled hands.   In Weimar[3] the method is recognised before the courts as legal.   Schmoeger,[4] of the dairy experiment station at Proskau, gets good results, although generally 0.2 per cent. too low.   Schulze and Krämer[5] consider the method to be as good as any for the quick determination of fat in milk, but they imply that something better is desirable.

The great practical value of so simple a method as this one under consideration for the determination of fat in milk, is not to be questioned ; and its usefulness to the dairyman or the milk inspector becomes very much enhanced by combination with Fleischman and Morgen's formula for calculating the per cent. of total solids, from the two known data, the specific gravity and the per cent. of fat ;[6] thus everything that needs to be known about a sample of milk for practical purposes can be learned with sufficient accuracy in a very short time, and without the use of a balance, the specific gravity being determined by a delicate areometer.   But in order that the method shall possess this value it is essential that it shall not be liable, under certain conditions of which the analyst might be in most cases quite ignorant, to such serious error as we have shown it to be in our own experience and that of others ; and it is most desirable, to say the least, that it should not be necessary, as is generally acknowledged by most of those who have tested the method, that even under ordinary conditions a possible error of

[1] Repertorium der analytischen Chemie **4**, 132.   [2] Journal für Landwirtschaft **32**, 197.

[3] Milch Zeitung **9**, 618.   [4] Journal für Landw. **29**, 129.

[5] Milch Zeitung **4**, 1415.   [6] Journal für Landwirtschaft **33**, 251.

0.2 to 0.3 must be granted, or from 7 to 8 per cent. of the total fat in average milk.

We offer the following contribution towards securing a greater degree of reliability in the use of the lactobutyrometer. Although we have not attained full success, we seem, so far as our results go, to have at least obviated the liability to error on account of the character of the ration on which the milk is produced.

The most important requisite for success is precise attention to the character of the reagents used. In the first place, Marchand directed that a few drops of sodium hydrate be first added to the milk. Schmidt and Tollens concluded that such addition was unnecessary, and omitted it in their directions; others, however,[1] hold that it is better to use this reagent. We have found it to be quite essential, at least in the examination of the milk of cows having bran or some other kinds of concentrated fodder in their ration ; and we have observed that, even when its addition is not necessary for this reason, still it is useful ; when used in sufficient quantity it prevents the formation of the abundant precipitate of casein that appears, in its absence, in consequence of the addition of the alcohol and the acetic acid, and in which some of the fat solution is liable to become entangled instead of continuing its course to the surface. Moreover, it appeared on microscopic examination of the milk that in the case of different samples the fat globules were unequally attacked by the ether when no alkali was used, and that this inequality disappeared in the presence of alkali ; in such presence solution of the fat takes place much more easily. Ammonia was found to answer this purpose as well as any other alkali, and at the same time there is less danger of any saponification of the fat, than if sodium or potassium hydrate or carbonate is used,[2] although, even with fixed alkali, no saponification could be detected in several careful trials. If, however, more than a very little fixed alkali is used, apparently a gelatinous albuminate is formed, which causes as much trouble as the precipitated casein, in entangling the ether-fat solution ; with ammonia no such difficulty appears.

In the second place, although Tollens and Schmidt mention the importance of maintaining certain relative proportions of alcohol and ether, our experience has shown that even more careful atten-

[1] Schulze and Krämer, *l. c.*   H. von Peter, *l. c.*   Vieth, Milch Zeitung **12**, 261.   Adam, Comptes Rendus **87**, 290.   Schmoeger, *l. c.*

[2] Christian, Technology of Soap and Candles, 74.

tion to this matter is necessary than they appear to require, for account must be taken of the alcohol in the ether itself, which in the case of ordinary ether is a variable quantity. It appears that, alkali being used as above mentioned, by maintaining an exact relation between the proportions of pure ether, alcohol, and water (of the milk), all of the fat and a portion of the ether will form together a very nearly definite mixture in the proportion of one part of the former to four of the latter ; this mixture rises to the surface and constitutes the layer of ether-fat solution which is measured in the lactobutyrometer ; but Marchand and others who have given directions for the process allow that a certain constant quantity of the fat remains in the liquid on which the ether-fat solution floats.

Absolute alcohol being miscible with both water and ether in all proportions, it is possible with a given quantity of ether and water to secure a complete mixture of these two unmiscible liquids, by the use of a certain quantity of alcohol. If with such a mixture a known quantity of pure butter fat be mixed, it can all be obtained again by careful, complete removal of the ethereal solution that collects at the surface, expelling the ether and drying and weighing the residue. This was proved by repeated trials. If for the quantity of water given milk be substituted, the ether-fat solution rising to the surface will consist of ether and fat only, and will contain all the fat of the milk, as was also proved by drawing off this solution and estimating the fat in it by weight. In fact, as has been proposed by Adam,[1] a method is hereby indicated, quicker than any yet given, for the gravimetric determination of fat in milk, the reliability of which we propose to test further.

The proper proportions of ether, alcohol and water (of the milk) necessary to secure the conveyance of all of the fat of the milk to the surface of the mixture in the form of an ether-fat solution containing very nearly one part of fat to four of ether, we have found by numerous trials to be 75 parts of pure ether, 100 of absolute alcohol and 135 of water. These proportions may be secured by mixing together 8 parts of Squibb's stronger ether, which contains 6 per cent. of 85 per cent. alcohol, 12 parts of 80 per cent. alcohol and 11 parts of water.

The following method of conducting the determination of the fat in milk with the lactobutyrometer, worked out in accordance

[1] Comptes Rendus **97**, 290.

with these principles, is proposed as a substitute for the method given by Schmidt and Tollens, which is, we believe, the one most generally followed.

The form of the instrument that we have used is represented in the adjoining figure. It is made of moderately thick-walled tubing (about 1 mm.) ; the stem is about 23 cm. and the bulb about 8 cm. long. It is important that the shoulder between the stem and the bulb should not be too abrupt. The bore of the stem is about 6 mm. and it is graduated in $\frac{1}{20}$ cc. The wider part of the tube has such a capacity that in passing from the lowest graduation on the stem to the inner end of the stopper in the lower mouth, one passes from 5 to 33 cc.; then the ether-fat solution will always come within the range of the graduation on the stem. This instrument differs from that originally given by Marchand, only in being open at the bottom as well as at the top ; this is a matter of some importance with reference to cleaning and drying it. The narrow stem in which the ether-fat solution collects makes more accurate readings possible than is the case with the wider tube with the same width of bore throughout, such as is now commonly used. These butyrometers were made for us by Emil Greiner, of New York.

Closing the lower mouth with a good cork, 10 cc. of the well mixed sample of milk are delivered into the well dried tube from a pipette, then 8 cc. of ether (Squibb's stronger) and 2 cc. of 80 per cent. alcohol. Close the smaller mouth of the tube with a cork, and mix the liquids by thorough shaking, which, however, need not be either violent or prolonged. Both corks should be held in place by the fingers during this operation, and the upper one should be once or twice carefully removed to relieve the pressure within, otherwise it is liable to be forced out suddenly unless carefully watched, with consequent danger of loss of material. Lay the tube on its side for a few minutes and then shake it again; add 1 cc. of ordinary ammonia diluted with about its volume of water, and mix as before by shaking; then add 10 cc. of 80 per cent. alcohol, and mix again thoroughly by moderate shaking, and holding the tube from time to time in an inverted position while the lighter portion of the liquid rises to the surface.

Now put the tube in water kept at 40° to 45°, till the ether-fat solution separates; this separation may be hastened by transferring the tube to cold water after it has stood in the warm water for a few minutes, and then returning it to the warm water. Finally transfer the tube to water kept at about 20° C., and as the level of the liquid falls in the stem by the contraction of the main body of it in the bulb, gently tap the side of the tube below the ether-fat solution, to dislodge any flakes of solid matter that may adhere to the walls; then as this solution finally takes its permanent position in the tube, its volume will not be increased by the presence of such foreign matters. The readings are to be taken from the lowest part of the surface meniscus to the line of separation between the ether-fat solution and the liquid below it.

The following table gives the percentages of fat corresponding to each tenth of a cubic centimetre of ether-fat solution down to 1 cc. and for each twentieth of a cubic centimetre thereafter.

Reading.		Per cent. of fat.	Reading.		Per cent. of fat.
3	...	1	13.5	...	3.51
4	...	1.23	14.0	...	3.63
5	...	1.47	14.5	...	3.75
6	...	1.71	15.0	...	3.87
7	...	1.95	15.5	...	4.00
8	...	2.19	16.0	...	4.13
9	...	2.43	16.5	...	4.26
10	...	2.67	17.0	...	4.39
10.5	...	2.79	17.5	...	4.52
11.0	...	2.91	18.0	...	4.65
11.5	...	3.03	18.5	...	4.78
12.0	...	3.15	19.0	...	5.01
12.5	...	3.27	19.5	...	5.14
13.0	...	3.39	20.0	...	5.27

This butyrometric method has been applied with fairly satisfactory results to the milk of a herd of cows receiving bran and cotton-seed meal in their ration. Equally good results have been obtained, usually with the milk of a single cow, whether having bran in her food or not, and with rich milk of Jersey cows. Of these results we give here only the last, when, at the same time, Soxhlet's well-known areometric method was taken into the comparison. In these tests the gravimetric determinations were made

by one of us by the convenient method devised by Dr. S. M. Babcock.[1] The milk is dried down on asbestos in a large test tube, with a small hole blown out at the bottom so that a current of air can be forced through it while in the drying bath. The quantity of asbestos taken is large enough to absorb 5 cc. of milk without dripping. The tube with its contents is then treated with ether in the usual manner in a fat extractor of the special form in use in this laboratory for several years.[2] The determinations by the butyrometer were made by one of the instructors in the laboratory who had not used the instrument before, and those by Soxhlet's method by another instructor. The results, including the duplicates, are given in the following table:

		Gravimetric.	Butyrometer.	Soxhlet.
I. Milk of the herd of cows. .	1	3.660	3.59	3.57
	2	3.657	3.57	3.59
II. " " " .	1	3.536	3.54	3.46
	2	3.539	3.52	3.41
III. Milk of cow having bran in her ration.	1	2.793	3.11	
	2	2.791	2.99	
IV. Milk of the herd.	1	3.305	3.31	3.23
	2	3.305	3.35	3.18
V. Milk of another cow having bran in the ration.	1	2.992	2.97	2.93
	2	2.992	2.99	2.96
VI. Milk of the same cow, another day.	1	3.053	3.38	2.98
	2		3.32	3.01

These results show that Marchand's butyrometric method as conducted by us is capable of a degree of accuracy that leaves nothing to be desired, and that in this respect it is not at all inferior to Soxhlet's method, while it is very much more simple, and can much more safely be put into unskilled hands. But, while so much can be claimed for it when applied to the mixed milk of a herd of several cows, more or less serious departures from such close agreement with the gravimetric results sometimes appear when the milk of a single cow is analysed, as shown in III ; but in this case, while the butyrometer gave tolerable results, Soxhlet's method failed entirely ; even after standing five hours, the layer of ether-fat solution in the mixing bottle, which should be over two centimetres thick, was hardly a millimetre thick. Of course no

[1] Second Report of the New York State Experiment Station, 1883, 169. [2] *Ibid.* 1880, 25.

reading could be taken of the specific gravity of this solution. This is not the first time that such a singular anomaly has been observed in working with this method. When the milk of another cow from the herd, having the same ration as III, was taken, while we obtained on one day excellent results by both the volumetric and the areometric methods, on the next day the volumetric method failed again to give perfect satisfaction.

Reserving further discussion of the subject till after the completion of the investigations, which are to be continued in this laboratory during the coming season, we will for the present simply say that we appear to have succeeded in so improving the method of analysis under consideration that at least useful results can be obtained under conditions of feeding of the cows, which before, in some way, caused the results to be utterly unreliable.

III. — A TEST OF CERTAIN METHODS FOR THE ESTIMATION OF THE SEVERAL ALBUMINOIDS IN COW'S MILK, AND OF THE INFLUENCE OF THE FOOD ON THE RELATIVE PROPORTIONS OF THESE ALBUMINOIDS.

By S. W. Parr.

The primary object of this investigation was to discover if possible the cause of certain difficulties encountered in this laboratory in the use of Marchand's lactobutyrometric method for the determination of fat in milk. It was undertaken at the suggestion of Prof. G. C. Caldwell and carried out under his supervision. A partial solution of the difficulties mentioned was reached from a somewhat different direction ; but the results of these experiments may possess some value for the information that they furnish in regard to the two points mentioned in the title of this paper.

The milk analysed was taken from a cow of common breed, about six years of age and six weeks in lactation. Three series of analyses were made, with reference to the albuminoids only, corresponding to three different rations, one of which contained no concentrated fodder. Each sample was analysed in duplicate, and also according to two different methods : first, for the total albuminoids by Ritthausen's method, of which a full description has

recently been given by Prof. Leeds in a paper on Woman's Milk;[1] second, for three forms of albuminoids in milk according to Pfeffer's method.[2]

In both methods dried and weighed filters were necessarily used; but by weighing the filters in short, large test-tubes, one of which had the rim cut off, and was just small enough to slide into the other, accurate results were obtained.

In the first method, for total albuminoids, as described by Prof. Leeds, the precipitation is accomplished by means of copper sulphate. The directions are to dry this precipitate " to a certain point," and pulverise before extracting the fat with ether. This point was found to be best attained by allowing the precipitate to drain thoroughly, or by drying it at a low temperature so that a crust shall not be formed on it. When in this cheesy form it was finely cut with a spatula and dried at 100° C.; then if double filters were used, by properly folding them so as to securely enclose the precipitate, it could be still further pulverised by pounding with a pestle upon a smooth surface.

The method for the estimation of the three different albuminoids need not be repeated here in full. The casein is precipitated by hydrochloric or acetic acid, the albumen by boiling, and the " third albuminoid " by tannic acid. The results of a number of analyses by these methods under the varying conditions of feed are given in the following table.

	Ration. Hay, Indian meal and Bran.		Ration. Hay.		Ration. Hay, Indian meal, Cotton-seed meal, Bran.	
Casein.	2.998	2.658	2.688	2.718	2.946	2.949
	2.500	2.558	2.748	2.706	...	2.819
	2.550	2.781	2.452	2.379	3.140	2.960
	...	...	2.564	2.555	3.220	3.200
Average.	2.683	2.666	2.613	2.589	3.102	2.982
Albumen.	.455	.462	.375	.300	.400	.42 ;
	.445	.480	.384	.395	.415	.528
	.443	.445	.384	.288	.456	.509
	...	...	.723	.284	.466	.460
Average.	.447	.462	.341	.317	.434	.480

[1] Chemical News **50**, 263.   [2] Fresenius, Zeitschrift für analyt. Chemie **22**, 14.

	Ration. Hay, Indian meal and Bran.		Ration. Hay.		Ration. Hay, Indian meal, Cotton-seed meal, Bran.	
3d albuminoid + tannin.	.392 .266 .252 ...	.417 .262 .290 ...	.246 .270 .280 .315	.208 .288 .288 .315	.280 .370 .269 .330	.285 .372 .249 .348
Average.	.303	.323	.278	.275	.312	.313
Sum.	3.433	3.451	3.232	3.181	3.848	3.775
Total albuminoids (Ritthausen's method).	3.218 2.925 2.988 3.193	3.178 2.945 3.045 3.205	2.912 2.705 2.778 3.065	2.854 2.654 2.838 3.043	3.378 3.451 3.403 3.273	3.497 3.408 3.434 3.163
Average.	3.081	3.093	2.865	2.847	3.376	3.375

With regard to these results it may be noted that for the total albuminoids, as determined by Ritthausen's method, the agreement between duplicates is very satisfactory; between different samples it is as close as could be expected, when it is considered how much the milk of the same cow may vary in composition from day to day. In the case of the sum of the three albuminoids determined separately the agreement is also close; but these total quantities exceed those obtained by Ritthausen's method by from 0.35 to 0.47 per cent., or a quantity closely approaching the percentages found of Pfeffer's third albuminoid.

The only evident source of error in these determinations of the separated albuminoids is one of excess; for this third albuminoid is weighed in the form of a precipitate containing an unknown quantity of tannin with the albuminous substance. On the other hand, it cannot be affirmed that the results obtained for the total albuminoids by Ritthausen's method are too low, for the reasons that the only evident source of error in this case would be the deduction of too large an amount of ash from the weight obtained of albuminoids plus non-volatile matter, owing to the uncertain and different combinations of the copper in the precipitate weighed and in the ash. The weight of ash deducted was 0.0727 gram; of this 0.061 gram was metallic copper, as calculated from the quantity of copper salt used in the precipitation. If to this last weight we add the actual casein ash found by analysis when no metallic base had been added, or 0.0112 gram, we have as the

sum 0.0722, which corresponds closely with the above deduction actually made. In burning the precipitated albuminoids with the filter-paper the copper is largely reduced to the metallic condition; in the precipitate it undoubtedly exists as a copper albuminate. It would appear from these considerations that we may fairly conclude that the method employed for the determination of the total albuminoids gives nearly, if not quite, correct results.

This throws upon the other method, in which the albuminoids are determined separately, the responsibility for the want of agreement between the two methods in the total results; at least a part of the error is due, as has been shown, to the method of estimating the residue of albuminous matter that is neither casein nor albumen.

Whether this method is accurate enough or not for the purpose of comparing different samples of milk produced under different conditions, must be decided by further experience; but it will be seen in the table, that while there is a marked difference, and always in the same direction, in the proportion of albumen, between the milk produced on hay alone, and that produced on the richer ration that preceded or followed it, which holds good for each sample, as well as for the averages of all the samples analysed on each ration, there is no such constant difference in respect to the "third albuminoid," although such a difference does appear, to a slight extent, in the averages of the results for this albuminoid; this notable difference appears also in the total albuminoids, by either method of determination, especially in passing from the hay to the following ration of hay and rich nitrogenous foods.

IV.—SOME NEW QUALITATIVE METHODS.

By Fred. A. Holton.

The Separation of Iodine and Bromine.—This separation is based on the fact that an alkaline iodide liberates free iodine in presence of potassium chromate and dilute nitric acid, while the bromide is not thus decomposed.

$$6NaI + 2K_2CrO_4 + 16HNO_3 =$$
$$Cr_2(NO_3)_6 + 6NaNO_3 + 4KNO_3 + 8H_2O + 6I.$$
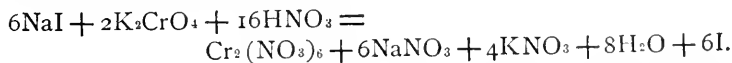
The operation is as follows: About 0.5 gram of the substance is boiled in 15 cc. of a saturated solution of sodium carbonate for a few minutes, and filtered. To 1 cc. of this solution containing the

iodine in the form of sodium iodide, dilute nitric acid (sp. gr. 1.156) is added in slight excess, then 2 or 3 drops of potassium chromate (8 of salt to 100 of water), and 1 cc. of carbon disulphide, and the whole is shaken thoroughly. The iodine is taken up by the carbon disulphide, and is removed by filtering through a moistened filter. To the filtrate 1 cc. of moderately strong chlorine water is added, and then $\frac{1}{2}$ cc. of carbon disulphide. After shaking, the brown color of bromine appears.

Too much potassium chromate is to be avoided, on account of the yellow color it imparts to the solution in which bromine is to be detected. This, however, may be obviated by diluting with water after shaking the last time.

Test for Chromic Acid.—This reaction between an iodide and a chromate, in the presence of free acid, serves as an extremely sensitive test for chromic acid. The solution to be tested having been boiled with sodium carbonate as above, to transpose the chromate, 1 cc. of this solution is slightly acidified with dilute hydrochloric acid (about 1.025 sp. gr.), and 1 or 2 drops of pure potassium iodide (1–10), and 0.5 cc. of carbon disulphide are added. A violet color appearing in the disulphide indicates chromic acid.

Arseniates, antimoniates, stannates, ferricyanides and chlorates also liberate iodine from the iodide under the above conditions. The interference of these acids may be obviated in the following manner : The sodium carbonate solution is made acid with acetic acid, a little barium chloride is added, the precipitate washed thoroughly, and then a little dilute hydrochloric acid is poured over the precipitate. The filtrate is now tested with potassium iodide and carbon disulphide as above.

To apply this test for *chromium*, in the precipitate of the hydrates of third and fourth group metals by barium carbonate, as obtained in the systematic course for analysis by Fresenius,[1] this precipitate is carefully washed free of nitrates by repeated decantation with hot water, a small portion of the residue is fused with pure sodium carbonate, boiled with a little water, filtered, the filtrate acidified with dilute hydrochloric acid, and brought nearly to boiling, two or three drops of oxalic acid are added to decompose any permanganate present, the solution is cooled completely, and tested with a drop or two of potassium iodide and 0.5 cc. carbon disulphide.

ITHACA, N. Y., *September*, 1885.

[1] Fresenius. Qualitative Analysis, Edition 1880, 295.

BENZOYLACETIC ACID AND SOME OF ITS DERIVATIVES.[1]

PART II.

BY W. H. PERKIN, Jun., Ph.D., *Privatdocent at the University of Munich.*

In Part I of this research I described the preparation and properties of ethylic benzoylacetate and of benzoylacetic acid, as well as of some compounds in which the hydrogen-atoms of the methylene group of the former are displaced by alcoholic radicles, such as ethyl-, diethyl-, and allyl-benzoylacetic ether, together with the products of their hydrolysis. Before describing the more complicated reactions in which ethylic benzoylacetate takes part, I should like to give the results of the experiments I have made with some of these compounds since the publication of Part I.

It has been found that although the substituted etheric salts of the benzoylacetic acids cannot be distilled without decomposition under the ordinary pressure, they can easily be obtained pure by distillation under diminished pressure. Using an apparatus similar to that described by Thorne, I have succeeded in purifying the monethyl- and allyl-derivatives described in the previous paper. If the crude product of the action of ethyl iodide on ethylic benzoylacetate is distilled under a pressure of 225 mm., a small quantity of acetophenone passes over first, and then the temperature rises rapidly to 220°, between which and 240° nearly the whole comes over as an almost colorless oil, leaving but a small residue. On repeatedly refractioning this oil under the same pressure, it distils mostly between 230–235°. The portion used for analysis boiled at 231–232° at 225 mm.

0.1550 gram substance gave 0.1020 gram H_2O and 0.4016 gram CO_2.

	Found.	Theory. $C_6H_5.CO.CH(C_2H_5).COOC_2H_5$.
C	70.66 per cent.	70.91 per cent.
H	7.31	7.27
O	22.03	21.82

Ethylic ethylbenzoylacetate is a colorless, strongly refracting oil possessing an aromatic odor and burning taste. When pure, it

appears to distil at the ordinary pressure almost without decomposition. The boiling points of the pure substance were incidentally noticed as being

$$210—211° \text{ at } 90 \text{ mm.}$$
$$223—224 \qquad 150$$
$$231—232 \qquad 225$$

Ethylic ethylbenzoylacetate is insoluble in potassic hydroxide solution, but appears to give a sodium compound on mixing it with sodic ethoxide. On continued boiling, no condensation-product is formed corresponding with the dehydrobenzoylacetic acid, which is so easily obtained by heating ethylic benzoylacetate for a short time by itself. This reaction I hope to describe in Part III of this paper. Ethylic acetoacetate and ethylacetoacetate behave in a precisely similar way. On passing ethylic acetoacetate through a tube at a dull red heat, it is almost completely decomposed, yielding as much as 20 per cent. of its condensation-product, dehydracetic acid, whereas ethylic ethylacetoacetate passes through almost unaltered, no trace of the analogous acid being formed.

Ethylic allylbenzoylacetate may also be purified in exactly the same way as ethylic ethylbenzoylacetate. On submitting the crude product of the action of allyl iodide on ethylic benzoylsodacetate to distillation under a pressure of 225 mm., nearly the whole passes over between 225–245° as a peculiar greenish-colored oil, with a slight reddish fluorescence. This coloration can only be removed by repeated fractioning, and even then it often returns on standing.

Pure ethylic allylbenzoylacetate boils at

$$220° \qquad \text{under } 100 \text{ mm. pressure.}$$
$$226—227° \qquad 130$$
$$240—241 \qquad 225$$

As it is difficult to burn, it is necessary that the combustion should be done with chromate of lead. The following numbers were obtained:

0.1491 gram substance gave 0.0902 gram H_2O and 0.3924 gram CO_2.

	Found.	Theory. $C_6H_5.CO.CH(CH_2.CH:CH_2).COOC_2H_5.$
C	71.77 per cent.	72.41 per cent.
H	6.72	6.89
O	21.51	20.69

Ethylic allylbenzoylacetate possesses the peculiar disagreeable odor characteristic of most allyl compounds. It does not solidify at 0°. The solution in acetic acid takes up bromine readily, especially if warmed, and without evolution of hydrobromic acid.

Ethylic benzoylacetate itself cannot be purified by distillation under diminished pressure, the greater part being decomposed, owing to the comparative slowness with which distillation takes place. When distilled as rapidly as possible (at 200 mm.) a portion passes over between 220-225°, consisting of nearly pure ethylic benzoylacetate, but a large residue is left containing considerable quantities of dehydrobenzoylacetic acid.

Having obtained ethylic monethyl- and allyl-benzoylacetates in a pure state, it was next thought necessary to repeat the hydrolysis with potash, in order, if possible, to obtain the acids in a pure state, but even when very dilute alcoholic potash was used, the acids were always mixed with benzoic acid, in some cases to a very considerable extent.

It was then thought that hydrolysis with sulphuric acid might give better results, and several experiments were therefore tried, using ethylic benzoylacetate itself in the first case.

On mixing ethylic benzoylacetate with twenty times its volume of concentrated sulphuric acid, and allowing it to remain for some time, the mixture becomes thick and dark-colored, small quantities of carbonic anhydride and sulphurous anhydride being given off.

After standing for fourteen days, the product was poured into ice water; this caused the precipitation of a thick dark brownish oil, which partly solidified on prolonged agitation. This uninviting body was separated from the aqueous solution by filtration, washed well with water, and then spread out on a porous plate; in this way the dark brown oil was almost completely removed from the crystals in two or three days, leaving them as a hard yellowish crystalline crust. After recrystallising it several times from warm benzene, the substance was easily obtained pure, melting between 103-104°, and presenting all the appearance of benzoylacetic acid.

On adding a drop of ferric chloride to the alcoholic solution, it gave the beautiful violet coloration mentioned in Part I, and the acid itself on dry distillation split up quantitatively into carbonic anhydride and acetophenone. There can be no doubt, therefore, that the substance was pure benzoylacetic acid. Experiments were next tried to ascertain if ethylic ethylbenzoylacetate could also be

hydrolysed in the same way. A small quantity of this ethereal salt was mixed with nearly three times its volume of concentrated sulphuric acid, and allowed to remain for three weeks. The solution became brownish-colored, but not nearly so dark as in the case of ethylic benzoylacetate itself; on adding water, an almost colorless oil was precipitated, which was removed by shaking with ether, and on evaporating the ether, a yellowish oil remained behind; this when exposed over sulphuric acid in a vacuum deposited crystals, apparently ethylbenzoylacetic acid. The quantity, however, was unfortunately too small for analysis, so that it will be necessary to repeat the experiment with more material before I can be certain that this method is of general application for the hydrolysis of ethylic benzoylacetate derivatives.

Part II of this research comprises the preparation and properties of ethylic nitrosobenzoylacetate, dibenzoylacetic acid, di- and tribenzoylmethane, the reduction of ethylic benzoylacetate, the action of phosphorous pentachloride on ethylic benzoylacetate, and the condensation of the latter with benzaldehyde.

Ethylic Benzoylnitrosoacetate.

By the action of nitrous acid on ethylic acetoacetate, Victor Meyer obtained ethylic nitrosoacetoacetate, according to the equation,

$$CH_3.CO.CH_2.COOC_2H_5 + NOOH =$$
$$CH_3.CO.C(N.OH).COOC_2H_5 + H_2O.$$

After a series of admirable researches, he proved that the formula of this compound was not $CH_3.CO.CH(NO).COOC_2H_5$, and therefore did not contain the nitroso-group NO, as was at first supposed, but that it was in reality an isonitroso-body, having the constitution $CH_3.CO.C(N.OH).COOC_2H_5$, and containing the isonitroso-radicle : N.OH.

With the exception of ethylic malonate, ethylic acetoacetate is the only compound which is capable of being converted into an isonitroso-derivative; for the substituted acetoacetates, such as ethylic ethylacetoacetate, $CH_3.CO.CH(C_2H_5).COOC_2H_5$, possessing only one hydrogen-atom which is capable of being substituted by any group, cannot combine with the dyad radicle NOH.

The nitroso-derivative of the whole molecule is therefore never formed by the action of nitrous acid on such bodies, but the

ethereal salt being first hydrolysed, carbonic anhydride is given off, and the nitroso-ketone remains behind :

$$CH_3.CO.CH(C_2H_5).COOC_2H_5 + NOOH =$$
Ethylic ethylacetoacetate.

$$CH_3.CO.C(C_2H_5):NOH + C_2H_5OH + CO_2.$$
Nitrosoethylacetone.

It therefore appeared interesting to try the action of nitrous acid on ethylic benzoylacetate and some of its derivatives, in order to determine whether they would follow the same law or not.

After several trials, the following was found to be the best method of preparing ethylic nitrosobenzoylacetate :

Ethylic benzoylacetate is first dissolved in dilute sodic hydroxide solution, filtered, mixed with an excess of sodic nitrite, and cooled down below 0° in a freezing mixture. Dilute sulphuric acid is then slowly added from a burette until the mixture is decidedly acid, care being taken that the liquid does not get warm. After a short time, more sodic hydroxide solution is added; this dissolves all that was precipitated by the sulphuric acid, producing an intense yellow solution, a sign that a nitroso-body has been formed. Last of all, the ethylic nitrosobenzoylacetate is precipitated by adding an excess of sulphuric acid. It separates as an oil, which, however, on agitating soon solidifies to long colorless needles. These are collected, well washed with water, and separated from any oily matter by spreading them out on a porous plate. In order to purify it, it is dissolved in a little hot alcohol, and water added until it becomes milky. The whole is then warmed up again and allowed to stand, when pure ethylic nitrosobenzoylacetate separates out in beautiful long colorless needles; on analysis, these gave the following numbers :

I. 0.1711 gram substance gave 0.0813 gram H_2O and 0.3729 gram CO_2.

II. 0.1566 gram substance gave 0.0730 gram H_2O and 0.3423 gram CO_2.

I. 0.2617 gram substance gave 16 cc. N, bar. $= 718$ mm., $t. = 21°$.

II. 0.2154 gram substance gave 12.5 cc. N, bar. $= 716$ mm., $t. = 18°$.

	Found.		Theory. $C_{11}H_{11}NO_4$.
	I.	II.	
C	59.44	59.62 per cent.	59.73 per cent.
H	5.28	5.18	4.97
N	6.56	6.31	6.33
O	28 72	28.89	28.96

From its analogy to ethylic nitrosoacetoacetate, this compound must have the formula $C_6H_5.CO.C(N.OH).COOC_2H_5$.

Ethylic nitrosobenzoylacetate melts at 120–121°. It is easily soluble in alcohol, ether, benzene, and chloroform, sparingly in water. It dissolves easily in alkalis, forming a yellow solution like all nitroso-bodies, and on acidifying is reprecipitated unchanged. It is decomposed by dry distillation with separation of charcoal and formation of hydrocyanic acid. A heavy oil passes over, which soon solidifies, and then melts at 110–114°; it is perhaps impure benzoic acid.

On treating ethylic nitrosoacetoacetate with alkalis, it is decomposed in the same way as ethylic acetoacetate itself, yielding nitrosoacetone instead of acetone. It was thought likely, therefore, that ethylic nitrosobenzoylacetate under the same conditions would give nitrosoacetophenone.

In order to test this, 3 grams of ethylic nitrosobenzoylacetate were dissolved in dilute potash, and allowed to remain for some days at the ordinary temperature, when the yellow solution of the nitroso-derivative became quite colorless. The product was then cooled in a freezing mixture, acidified with sulphuric acid, and extracted with ether. On evaporating the ethereal solution, it deposited a colorless crystalline substance, which contained but traces of nitrogen, and therefore could not be nitrosoacetophenone. It is easily soluble in warm water, and on cooling crystallises in small thick prisms, which were collected, dried over sulphuric acid in a vacuum, and analysed, with the following results:

I. 0.1797 gram substance gave 0.0684 gram H_2O and 0.3962 gram CO_2.

II. 0.1247 gram substance gave 0.0477 gram H_2O and 0.2747 gram CO_2.

	Found.		Theory.
	I.	II.	$C_9H_8O_4$.
C	60.13	60.08 per cent.	60.00 per cent.
H	4.22	4.25	4.44
O	35.65	35.67	35.55

The compound therefore appears to have the formula $C_9H_8O_4$. It crystallises from water in small prisms melting at 125°. It dissolves easily in alkalis, forming a colorless solution. On precipitating the neutral solution of the ammonium salt with silver nitrate, the silver salt was obtained as a voluminous white pre-

cipitate, which, after being dried over sulphuric acid in a vacuum, gave the following numbers on analysis :

0.3050 gram substance gave 0.1147 gram $Ag = 37.61$ per cent.

Theory, $C_9H_7O_4Ag = 37.63$

I hope at some future time to be able to examine more thoroughly this curious reaction, and if possible to determine the constitution of the body $C_9H_8O_4$.

Dibenzoylacetic Acid.

In the preceding chapters it has been shown that ethylic benzoylacetate is capable of forming derivatives in which the hydrogen-atoms of the methylene group are displaced by alcoholic radicles such as ethyl, allyl, etc., in exactly the same way as ethylic acetoacetate. It was thought likely that very interesting results might be obtained if the acid chlorides, such as benzoyl chloride, were substituted for the iodides of the alcoholic radicles in the above reaction. If the sodium compound of ethylic benzoylacetate be heated with benzoyl chloride, the ethyl salt of dibenzoylacetic acid is formed according to the equation,

$C_6H_5.CO.CHNa.COOC_2H_5 + C_6H_5COCl =$

$(C_6H_5.CO)_2.CH.COOC_2H_5 + NaCl.$
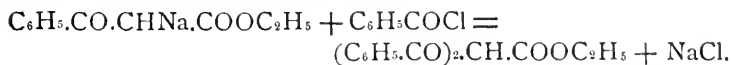
This ethereal salt on hydrolysis gives dibenzoylacetic acid,

$(C_6H_5.CO)_2CH.COOH.$

When boiled with dilute acids, dibenzoylacetic acid is easily split up into acetophenone, benzoic acid, and carbonic anhydride, thus,

$(C_6H_5.CO)_2CH.COOH + H_2O =$

$C_6H_5.CO.CH_3 + C_6H_5.COOH + CO_2.$
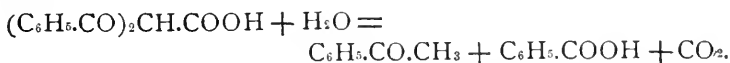
If boiled with water, a second reaction takes place at the same time, by which dibenzoylmethane is formed according to the equation,

$(C_6H_5.CO)_2CH.COOH = (C_6H_5.CO)_2CH_2 + CO_2.$
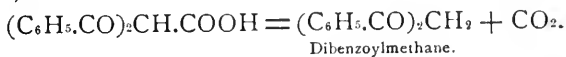
Dibenzoylmethane.

In the preparation of ethylic dibenzoylacetate it is not necessary to use the pure dry sodium compound of ethylic benzoyl-acetate and act on it with benzoyl chloride in ethereal solution, as was done in the first experiments, but we may proceed in the way usually employed in such syntheses, that is, by mixing ethylic benzoylacetate with sodic ethylate, and allowing benzoyl chloride

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to act directly on the product in the following way : 0.6 gram of sodium is dissolved in absolute alcohol, well cooled, and then mixed with 4 grams of ethylic benzoylacetate. 3 grams of benzoyl chloride are now added drop by drop, the whole being well cooled in a mixture of ice and salt. The reaction is very energetic, each drop of benzoyl chloride instantly producing a precipitate of chloride of sodium, and so much heat is developed that the alcohol will boil if a refrigerating mixture is not used. After all the benzoyl chloride has been added, the whole is warmed on a water-bath for about a quarter of an hour to insure the reaction being complete, and the greater part of the alcohol is distilled off; water is then added, and the product allowed to remain for some time, in order to insure the decomposition of any slight excess of benzoyl chloride. The watery liquid is next extracted with ether once or twice, the ethereal solution well shaken with carbonate of soda to remove benzoic acid, dried over potassium carbonate, and the ether distilled off. A thick dark brown oil remains behind. This was not further purified, although it is possible that by fractioning in a vacuum the ethylic dibenzoylacetate might be obtained in a pure state, as in the case of the ethyl- and allyl-benzoylacetates.

In order to obtain the free acid, the crude ethereal salt was hydrolysed by warming with an excess of alcoholic potash for about ten minutes on a water-bath. The mixture became dark colored, and on adding water almost all of it dissolved, forming a dark brownish solution ; this when acidified deposited the crude dibenzoylacetic acid as a thick oil, which became nearly solid on agitating for a short time. The product was collected, well washed with water, and dissolved in as little boiling alcohol (80 per cent.) as possible. On cooling, the acid crystallised out in colorless nodules, and was easily obtained pure and free from benzoic acid by repeated crystallisation. On analysis the following numbers were obtained :

0.2257 gram substance gave 0.0925 gram H_2O and 0.5926 gram CO_2.

	Found.	Calculated, $C_{16}H_{12}O_4$.
C	71.61 per cent.	71.64 per cent.
H	4.55	4.48
O	23.84	23.88

This substance was therefore dibenzoylacetic acid,

$$(C_6H_5.CO)_2CH.COOH.$$

The acid melts at 109°. When rapidly heated in small quantities, some of it distils undecomposed, but the greater part is split up into dibenzoylmethane and carbonic anhydride according to the equation,

$$(C_6H_5CO)_2.CH.COOH = CH_2(CO.C_6H_5)_2 + CO_2.$$

Dibenzoylacetic acid.   Dibenzoylmethane.
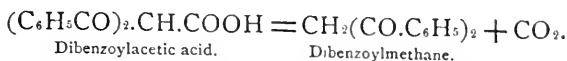
Dibenzoylacetic acid is sparingly soluble in water and cold alcohol, but easily so in hot alcohol, benzene, and ether. The solution in alcohol gives a dirty red coloration on the addition of ferric chloride. The acid dissolves in concentrated sulphuric acid, producing a yellow solution, which, however, becomes colorless on warming. It dissolves slowly in solutions of ammonia, sodic hydroxide, and sodic carbonate, and is reprecipitated on the addition of an acid. In order to obtain a neutral solution of the ammonium salt, the pure acid was dissolved in a slight excess of dilute ammonia, and then allowed to stand over sulphuric acid in a vacuum until the excess of ammonia had evaporated. The salt itself is very easily soluble in water; on boiling the solution carbonic anhydride is given off, and the smell of acetophenone becomes noticeable. Several of the salts of dibenzoylacetic acid were prepared by precipitating the solution of the ammonium salt with various reagents. The *silver salt* is obtained on adding a solution of nitrate of silver as a white curdy precipitate, sparingly soluble in water. For analysis, the substance was dried at 80°.

0.1154 gram substance gave 0.0327 gram silver.

	Found.	Theory. $(C_6H_5CO)_2CH.COOAg.$
Ag	28.34 per cent.	28.72 per cent.

A solution of cupric sulphate precipitates the *copper salt* as a light yellowish-green mass, which appears to be somewhat soluble in hot water and alcohol. Prolonged boiling, however, decomposes the salt, cupric oxide being precipitated. This copper salt dissolves easily in ammonia, yielding a beautiful blue solution. The *barium salt* is soluble in water, and is prepared by shaking the finely powdered acid with baryta-water and a little alcohol for some time. After precipitating the excess of baryta by passing carbonic anhydride and filtering, a solution of the salt is obtained, which, however, is partly decomposed by evaporation. The *zinc salt* is also easily soluble in water. With a solution of the ammonium salt, acetate of lead gives a white curdy precipitate of the *lead salt.*

With a solution of sulphate of nickel, the *nickel salt* is obtained as a light green precipitate soluble in excess of sulphate of nickel. Ferric chloride gives a brownish-red coloration with dilute solutions of the ammonium salt; with more concentrated solutions, however, the *ferric salt* is precipitated as a dirty reddish precipitate somewhat soluble in hot water. Ferrous sulphate gives the same reaction. Chloride of tin precipitates the *tin salt* as a heavy white mass sparingly soluble in water.

If dibenzoylacetic acid is mixed with alcoholic potash, a yellowish-green solution is formed which is decomposed by boiling, benzoic acid and a neutral body being formed. On distilling dibenzoylacetic acid with soda-lime it is split up into benzene and an oily substance, which appears to be acetophenone.

In order to obtain pure ethylic dibenzoylacetate, the pure acid was dissolved in absolute alcohol, and hydrogen chloride passed through the solution until it was thoroughly saturated, the whole being kept well cooled during the operation. On adding water, an oil was precipitated, which, on distillation, came over almost entirely between 205–220° as a colorless oil smelling strongly of ethyl-benzoate. The pure ether can easily be prepared, however, by decomposing the silver salt of the acid with ethylic iodide in ethereal solution. After filtering from the precipitated iodide of silver and evaporating on a water-bath, ethylic dibenzoylacetate remains behind as a thick colorless oil of a faint fruity odor; it does not solidify when cooled down to —10°.

Several experiments were next made in the hope of obtaining tribenzoylacetic acid by treating ethylic dibenzoylacetate with sodic ethylate and benzoyl chloride as expressed in the equation,

$$(C_6H_5.CO)_2CNa.COOC_2H_5 + C_6H_5.COCl =$$
$$(C_6H_5.CO)_3C.COOC_2H_5 + NaCl.$$
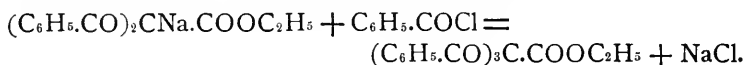
In this way an almost colorless oil is obtained, which, however, is unfortunately completely split up on hydrolysis, nothing but benzoic acid being formed.

As it appeared probable that ethylic tribenzoylacetate was really formed in the first place, an experiment was very carefully made with pure ethylic dibenzoylacetate, and the product, freed from excess of benzoyl chloride and benzoic acid by shaking with dilute sodic carbonate, was dried over carbonate of potash and analysed.

	Found.	Theory. $(C_6H_5.CO)_3C.COOC_2H_5.$	Theory. $(C_6H_5.CO)_2CH.COOC_2H_5.$
C	74.19 per cent.	75.00	72.97 per cent.
H	4.91	5 00	5.41
O	21.00	20.00	21.62

This ethereal salt is a very thick yellowish oil, which unfortunately could not be made to crystallise. On boiling it with dilute sulphuric acid, acetophenone and a solid acid, probably benzoic acid, are formed. It dissolves in alcoholic potash and is reprecipitated on adding a few drops of water, whereas ethylic dibenzoylacetate is only precipitated from its solution in alcoholic potash on the addition of a much larger quantity of water.

DECOMPOSITION-PRODUCTS OF DIBENZOYLACETIC ACID.

Dibenzoylmethane.

As dibenzoylacetic acid contains two carbonyl-groups, it seemed probable that interesting results might be obtained by carefully examining its decomposition-products. The acid was therefore treated with several reagents; first of all with dilute sulphuric acid in the hope of simply splitting off carbonic anhydride, and thus obtaining dibenzoylmethane according to the equation,

$$(C_6H_5.CO)_2CH.COOH = CO_2 + CH_2(CO.C_6H_5)_2.$$
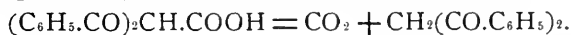
The experiment was carried out in the following way: A mixture of pure dibenzoylacetic acid with an excess of dilute sulphuric acid (1 : 2) was heated for about five hours in a flask connected with a reflux condenser; at the end of this a test-tube containing baryta-water was fixed, to serve as a rough indicator both of the quantity of carbonic anhydride and the rate at which it was given off.

The acid soon began to decompose, and swam about in the liquid at first as a semi-solid mass, but later on in large oily drops, a considerable quantity of carbonic anhydride being evolved. At the end of the reaction, the contents of the flask, which smelt strongly of acetophenone, were subjected to distillation by steam; in this way a considerable quantity of a colorless oil passed over and was extracted by shaking with ether. On distilling off the ether and subsequent fractioning, nearly the whole of the residual oil passed over between 195–205°, and without doubt consisted of nearly pure acetophenone. In order to be certain it was shaken with a solution of orthonitrobenzaldehyde in dilute sodic hydroxide,

when a considerable quantity of indigo was precipitated after the mixture had been standing for some time.

On cooling, the residue in the flask deposited a quantity of glittering crystals which were collected and dried. They melted at 120° and showed all the properties of benzoic acid, with which they were no doubt identical.

Dibenzoylacetic acid is therefore decomposed by boiling with dilute sulphuric acid into benzoic acid, carbonic anhydride, and acetophenone according to the equation,

$$(C_6H_5.CO)_2CH.COOH + H_2O =$$
$$C_6H_5.COOH + C_6H_5.CO.CH_3 + CO_2.$$
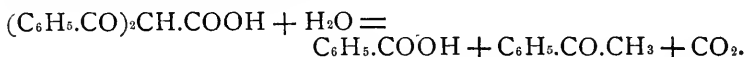
In repeating this reaction more carefully, it was noticed that if the boiling with sulphuric acid were stopped before all the dibenzoylacetic acid had been decomposed, a small quantity of a solid body, insoluble in sodic carbonate, could be isolated; when this is dissolved in alcohol and ferric chloride added, it gives a beautiful reddish-violet coloration. As, however, only very small quantities of this compound could be obtained by this method, several experiments were tried in order to improve the yield, and it was found that simple boiling with distilled water gave the desired result.

Pure dibenzoylacetic acid was boiled with water in a flask connected with a reflux condenser as long as carbonic anhydride continued to come off in any quantity (about 4–5 hours).

The acid melted slowly and sank to the bottom of the flask as a heavy, slightly brownish oil, which on cooling partially solidified, the liquid becoming filled with needles of benzoic acid. A dilute solution of sodic carbonate was now added, and the whole well shaken and allowed to stand for some time until all the benzoic acid had dissolved. After filtering and washing with water a small quantity of a semi-solid mass remained, smelling strongly of acetophenone; the latter can be roughly separated from the crystals by spreading them out on a porous plate or by pressing between blotting-paper. The crude product thus obtained was then dissolved in a little hot methyl alcohol, from which it crystallised on cooling in beautiful flat plates; these are easily obtained pure by recrystallisation.

The analysis gave numbers agreeing with the formula,

$$CH_2(CO.C_6H_5)_2.$$

0.1967 gram substance gave 0.0952 gram H_2O and 0.5772 gram CO_2.

	Found.	Calculated, $CH_2(CO.C_6H_5)_2$.
C	80.03 per cent.	80.36 per cent.
H	5.37	5.36
O	13.60	14.28

This compound was therefore dibenzoylmethane or benzoylaceto-phenone. It melts at 81° and distils above 200°, apparently without the least decomposition. It is easily soluble in ether, alcohol, and chloroform, the alcoholic solution, on the addition of a drop of ferric chloride, giving an intense reddish-violet coloration which resembles very closely that produced by benzoylacetic acid itself. If the solution in hot methyl alcohol is cooled slowly, it crystallises most beautifully; it can, however, best be obtained in large crystals by allowing the ethereal solution to evaporate slowly. Professor Haushofer was kind enough to measure these crystals, and gave me the following description of them:

Crystalline system rhombic:

$$a:b:c = ?:1:1.38.$$

Small crystals with rhomboidal base and extended in the direction of the makrodiagonal on which the surface oP (c), $\infty \bar{P}\infty$ (a), $\breve{P}\infty$ (r), and an undetermined makrodome, d, were observed. The only surfaces fit for measurement were a, r, and in some crystals c.
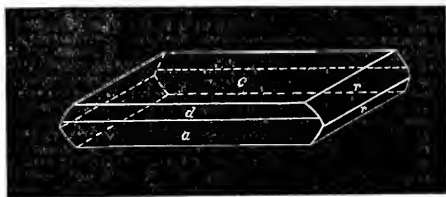
The surface d is smooth, curved, and appears only on one-half of the crystals (with respect to the basal section). The surface c is also generally curved.

	Measured.	Calculated.
$r:r$	108° 18′	...
$c:r$	125° 54′	125° 51′
$a:r$	90°	90°

The compound is remarkable by the strong dispersion in its axes. The medial line is the vertical axis. The makropinacoïd is the

plane of the optical axis for the red, and the brachypinacoïd for the blue. In the polariscope with white light, the surface c shows the interference figure of rhombic titanic acid (brookite).

Dibenzoylmethane is easily soluble in alkalis, particularly in alcoholic potash, and is reprecipitated unchanged on acidifying. It combines easily with phenylhydrazine, forming a solid substance, which, however, was not further examined.

Tribenzoylmethane.

Dibenzoylmethane, $CH_2(CO.C_6H_5)_2$, contains a methylene-group associated with two carbonyl-groups, and for this reason is soluble in alkalis, forming metallic salts, the methylene-group in this body behaving in exactly the same way as the corresponding one in ethylic benzoylacetate, $C_6H_5.CO.CH_2.COOC_2H_5$. It appeared probable, therefore, that by further treatment with sodic ethylate and benzoyl chloride a tribenzoylmethane might be formed according to the equation,

$$CHNa(CO.C_6H_5)_2 + C_6H_5.COCl = CH(CO.C_6H_5)_3 + NaCl.$$

This is in reality the case, as will be seen from the following experiment: 2 grams of pure dibenzoylmethane were mixed with a solution of 0.2 gram of sodium in absolute alcohol, and then as soon as all had completely dissolved, 1.4 gram of benzoyl chloride was added drop by drop. Sodic chloride was immediately precipitated, the mixture becoming warm. After all the benzoyl chloride had been added, the product was heated on a water-bath for about ten minutes to ensure the reaction being complete; a quantity of water was then added, when a solid body separated; this was collected, well washed with water, and spread out on a porous plate to remove a small quantity of oil adhering to the crystals.

The compound was easily purified by recrystallisation from alcohol, and gave the following numbers on analysis:

0.1849 gram substance gave 0.0864 gram H_2O and 0.5443 gram CO_2.

	Found.	Theory, $CH(CO.C_6H_5)_3$.
C	80.28 per cent.	80.49 per cent.
H	5.19	4.87
O	14.53	14.63

This substance, therefore, is tribenzoylmethane. On heating it melts at 224–225°, and sublimes at a higher temperature almost

without decomposition ; in this respect it seems to be an extremely stable compound. Tribenzoylmethane is almost insoluble in cold alcohol, more easily soluble in hot, and crystallises from this solvent on cooling in small, almost microscopic, colorless needles. The hot alcoholic solution gives an orange coloration on adding a drop of ferric chloride. It is fairly easily soluble in benzene and carbon bisulphide, and crystallises in small needles on evaporating the solution. In chloroform and ether, on the contrary, it is sparingly soluble, and in light petroleum almost insoluble. It dissolves readily in alcoholic potash, and on adding water forms a colorless solution from which acids precipitate the original compound unchanged. On warming with concentrated sulphuric acid it is colored yellow. Nitric acid appears to entirely decompose it. Experiments were next made in the hope of obtaining tetrabenzoylmethane by the further action of sodic ethylate and benzoyl chloride on tribenzoylmethane, thus:

$$CNa(CO.C_6H_5)_3 + C_6H_5.COCl = C(CO.C_6H_5)_4 + NaCl.$$

By this means a small quantity of a colorless body was obtained which, after being extracted several times with boiling alcohol, melted between 260–270°, and gave the following results on analysis :

	Found.	Theory, $C(C_6H_4CO)_4$.	Theory, $CH(C_6H_5CO)_3$.
C	81.43 per cent.	80.58 per cent.	80.49 per cent.
H	5.15	4.63	4.87
O	13.42	14.80	14.63

As will be seen from the above, the analysis of such a substance does not show whether it is a tetra- or tri-benzoylmethane. The only fact which seems to prove that tetrabenzoylmethane had been formed is that the product is far more sparingly soluble in alcoholic potash than tribenzoylmethane. I hope at some future time to be able to continue the study of these interesting compounds, and if possible to improve the methods of preparing them.

Reduction of Ethylic Benzoylacetate.

Benzoylacetic acid being a ketonic acid, it was thought that it would be interesting to study the action of nascent hydrogen on it, in order, if possible, to obtain β-phenyllactic acid according to the equation,

$$C_6H_5.CO.CH_2.COOH + H_2 = C_6H_5.CH(OH).CH_2.COOH.$$
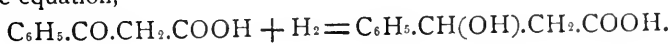
In this reaction it is better to use ethylic benzoylacetate than the free acid ; the following method gives good results.

Ethylic benzoylacetate is dissolved in dilute sodic hydroxide solution, care being taken to avoid any large excess of alkali, and then 5 per cent. sodium amalgam is added in small portions at a time. The amalgam liquefies at first without evolution of hydrogen, the liquid becoming so warm that it is necessary to cool it continually. After about ten hours, hydrogen begins to be evolved, and the reaction is finished. The product is then filtered from a small amount of a resinous body (which will be described later on), the filtrate acidulated with dilute sulphuric acid, and extracted several times with ether. On distilling off the ether, an almost colorless oily acid remains, which does not solidify even after long standing in a vacuum over sulphuric acid. In order to purify it, the whole is converted into the barium salt by agitation with baryta-water, the excess of baryta removed by carbonic anhydride, and the precipitated barium carbonate filtered off. The colorless solution of the barium salt of the acid so obtained is acidified with hydrochloric acid, shaken several times with ether, and the ethereal solution dried over chloride of calcium. On distilling off the ether, a very thick colorless oil is left; and this, on standing for some time, solidifies almost completely, especially after scratching the sides of the vessel containing it with a sharp glass rod. It may be purified by crystallising it once or twice from benzene, when it is obtained in beautiful colorless nodules consisting of fine needles. It melts at 93–94°, and gave the following numbers on analysis :

0.2005 gram substance gave 0.1100 gram H_2O and 0.4760 gram CO_2.

	Found.	Theory. $C_6H_5.CH(OH).CH_2.COOH.$
C	64.75 per cent.	65.06 per cent.
H	6.09	6.03
O	21.16	28.91

The substance was therefore β-phenyllactic acid, and was further identified by an analysis of the silver salt, which is easily obtained by precipitating a neutral solution of the ammonium salt with nitrate of silver, as a white curdy precipitate, somewhat soluble in water.

0.3360 gram substance gave 0.1330 gram $Ag = 39.58$ per cent.
Theory, $C_6H_5.CH(OH).CH_2.COOAg = 39.56$

On heating this silver salt it decomposes into silver carbonic anhydride and cinnamene, almost without charring. The acid itself, when carefully heated, splits up almost quantitatively into water and cinnamic acid, according to the equation,

$$C_6H_5.CH(OH).CH_2.COOH = C_6H_5.CH:CH.COOH + H_2O.$$
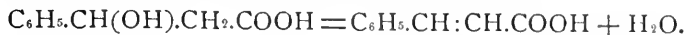
This acid has all the properties of the β-phenyllactic acid prepared by Glaser[1] by the action of sodium amalgam on phenylchlorolactic acid, $C_6H_5.CH(OH).CHCl.COOH$, its formation from ethylic benzoylacetate being a proof that the hydroxyl group is really in the β-position. The same acid is also formed by boiling phenylbromopropionic acid, $C_6H_5.CHBr.CH_2.COOH$, with water.[2]

By the action of nascent hydrogen on ethylic benzoylacetate there is always a certain amount of a resinous substance formed, which separates out of the alkaline solution during the reduction, and can easily be freed from the sodic salt of the β-phenyllactic acid by filtration and washing with water. As in some cases a considerable amount of this compound was formed, it was thought that it might contain something definite, and was therefore carefully examined. The filter-papers were extracted with ether, and the ethereal solution filtered and evaporated; by this means a very thick dark-brown oil was left behind, which, after standing for several days, partly crystallised. The crystals were easily obtained colorless and free from oil, by repeated washings with small quantities of ether in which they are difficultly soluble. Last of all they were dissolved in a little hot alcohol, from which they crystallise on cooling in thick colorless prisms melting at 102°.

The analysis gave the following result:

I. 0.1665 gram substance gave 0.0768 gram H_2O and 0.4581 gram CO_2.

II. 0.2082 gram substance gave 0.0906 gram H_2O and 0.5720 gram CO_2.

	Found.		Theory, $(C_5H_4O)_n$.
	I.	II.	
C	75.04	74.93 per cent.	75.00 per cent.
H	5.12	4.83	5.00
O	19.84	20.24	20.00

This substance therefore has the formula $(C_5H_4O)_n$, most likely $C_{10}H_8O_2$.

[1] Annalen **147**, 86.   [2] Fittig and Binder, Annalen **195**, 138.

When warmed with alcoholic potash it yields an intense magenta-red solution ; and on filtering and acidifying, a colorless crystalline acid is precipitated. The alcoholic solution does not give any color reaction with ferric chloride.

A small quantity of this body warmed with concentrated sulphuric acid dissolves, forming a pinkish solution with a slight greenish fluorescence. If, after standing for a short time, this solution be poured into water, a whitish amorphous substance separates ; this forms an intense blue-green solution on the addition of an excess of sodic hydroxide. If the original substance, however, be more strongly heated with sulphuric acid, the pinkish color first produced becomes browner, and at last of a deep olive-green. On pouring this olive-green solution into water, a bright yellowish liquid is produced, which, on the addition of sodic hydroxide, becomes of a beautiful purple. This reaction is extremely delicate, and is produced by mere traces of substance. This compound is isomeric with a substance which was obtained by the action of sodium on acetate of phenyl, a reaction which W. R. Hodgkinson and I studied some time ago.[1] Curiously enough the latter also gives the same characteristic reaction when warmed with potash ; the red color is destroyed, however, on diluting with water, which is not the case with the body described above.

Action of Phosphorous Pentachloride on Ethylic Benzoylacetate.

Geuther,[2] who was the first to study the action of pentachloride of phosphorus on ethylic acetoacetate, found that when it was treated with an excess of the former it was resolved into the chlorides of two isomeric chlorcrotonic acids, namely, β-chlor-α-crotonic acid, $CH_3.CCl : CH.COOH$, and the β-chloro-β-crotonic acid, $CH_2 : CCl.CH_2.COOH$.

On decomposing these chlorides with water, and distilling with steam, the β-chloro-β-crotonic acid distils over first, and then the β-chlor-α-crotonic acid. As the methyl group of the ethylic acetoacetate must have taken part in the formation of β-chloro-β-crotonic acid, supposing the formula $CH_2 : CCl.CH_2.COOH$ to be correct, it appeared interesting to repeat these experiments with ethylic benzoylacetate, in which the presence of the phenyl group would shut out the possibility of the formation of any acid analogous in constitution to β-chloro-β-crotonic acid.

[1] Journal of the Chemical Society. Transactions **37**, 487.   [2] Zeitschr. f. Chem. 1871, 237.

In order to test this, 10 grams of ethylic benzoylacetate were dissolved in 25 grams of oxychloride of phosphorus, and 25 grams of phosphorous pentachloride slowly added. As the reaction appeared to take place very slowly at ordinary temperatures, the mixture becoming only slightly warm, the whole was heated for about half an hour on a water-bath, when the pentachloride slowly disappeared, hydrogen chloride being given off. As soon as the reaction was over the oxychloride of phosphorus was distilled off on a water-bath in a vacuum, the latter portions carrying over a small quantity of a crystalline substance which sublimed into the condenser in yellow needles ; these, however, were not further examined. The residue, consisting of a dark-brown oil, was poured into ice-water and allowed to remain for some time, in order that acid chlorides and any excess of pentachloride of phosphorus might be entirely decomposed. An excess of sodic carbonate was then added, and the whole gently warmed with animal charcoal on a water-bath for about fifteen minutes, and filtered. On acidifying the filtrate, which was nearly colorless, it deposited a crystalline acid ; this was collected, well washed, and recrystallised twice from alcohol. It was thus obtained perfectly pure in beautiful glittering plates, which, on analysis, gave the following result :

0.1798 gram substance gave 0.0665 gram H_2O and 0.3901 gram CO_2.

0.2424 gram substance gave 0.3080 AgCl.

	Found.	Theory, $C_9H_7O_2Cl$.
C	59.17 per cent.	59.18 per cent.
H	4.10	3.84
Cl	19.47	19.45
O	17.26	17.53

The compound was therefore chlorocinnamic acid, produced according to the equations,

I. $C_6H_5.CO.CH_2.COOC_2H_5 + 2PCl_5 =$
$C_6H_5.CCl_2.CH_2.COCl + C_2H_5Cl + 2POCl_3$.

II. $C_6H_5.CCl_2.CH_2.COCl + H_2O =$
$C_6H_5.CCl:CH.COOH + 2HCl$.
β-Chlorocinnamic acid.
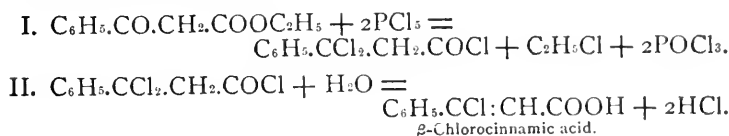
By this reaction, therefore, β-chlorocinnamic acid should be obtained. There are two monochlorocinnamic acids known, the

a-monochlorocinnamic acid, $C_6H_5.CH:CCl.COOH$, and the β-monochlorocinnamic acid, $C_6H_5.CCl:CH.COOH$. These were obtained by Jutz[1] in a way exactly similar to that employed by Glaser[2] in the preparation of the monobromocinnamic acids, namely, by heating phenyldichloropropionic acid with potash :

2. $C_6H_5.CHCl.CHCl.COOH + 4KOH =$
Phenyldichloropropionic acid.

$C_6H_5.CH:CCl.COOK$
Potassic a-chlorocinnamate.

$+ C_6H_5.CCl:CH.COOK + 2KCl + 4H_2O.$
Potassic β-chlorocinnamate.
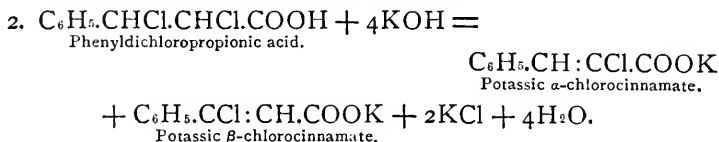
He separated these acids by means of the potash salts, the salt of the a-acid being sparingly soluble in water, whereas the salt of the β-acid is easily soluble. The a-chlorocinnamic acid, crystallised from water, melts at $137-138°$, crystallised from light petroleum at $142°$. β-Chlorocinnamic acid melts at $114°$. a-Chlorocinnamic acid is also formed by heating phenylchlorolactic acid with water at $120-200°$:

$C_6H_5.CH(OH).CHCl.COOH = C_6H_5.CH:CCl.COOH + H_2O.$
Phenylchlorolactic acid. a-Chlorocinnamic acid.
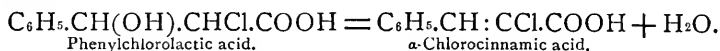
This is a proof that the chlorine is in the a-position, there being no doubt as to the constitution of phenylchlorolactic acid. A further proof of the constitution of a-chlorocinnamic acid is its formation by the action of acetic anhydride on a mixture of benzaldehyde with sodic monochloracetate, according to the equation,[3]

$C_6H_5.COH + CH_2Cl.COONa = C_6H_5.CH:CCl.COONa + H_2O.$
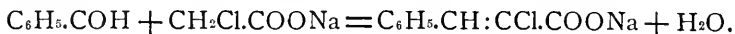
The chlorocinnamic acid obtained from ethylic benzoylacetate by the action of pentachloride of phosphorus in the way just described, melts at $142°$, and possesses, strangely enough, all the properties of a-chlorocinnamic acid, with which it is no doubt identical, although, according to the equation given above, β-chlorocinnamic acid should be produced.

The formation of a-chlorocinnamic acid from ethylic benzoylacetate in this way is difficult to explain ; one is forced to come to the conclusion that the β-acid is first formed, and afterwards, under the influence of such powerful reagents as pentachloride and oxychloride of phosphorus, that a molecular change takes place, whereby the β-acid is transformed into the a-acid. In the case of

[1] Berichte **15**, 788.   [2] Annalen **143**, 330.   [3] Plöchl, Ber. **15**, 1945.

the monobromocinnamic acids, the β-acid can with the greatest ease be transformed into the α-acid by distillation, or by heating with hydriodic acid, the change being almost quantitative. Still stranger is the fact that the β-monobromocinnamic acid on etherification is converted quantitatively into the ethyl salt of α-monobromocinnamic acid. This mobility of the bromine-atom makes it appear possible that these compounds are merely physical isomerides, and not chemical isomerides in the true sense of the word.

Condensation of Ethylic Benzoylacetate with Benzaldehyde.

The hydrogen-atoms of the methylene group in ethylic acetoacetate are very easily substituted by condensation with aldehydes, according to the equation,[1]

$$CH_3.CO.CH_2.COOEt + R.CHO =$$
$$CH_3.CO.C(: CH.R).COOEt + H_2O.$$
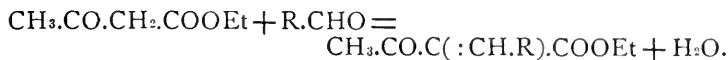
This condensation is best brought about by mixing the ethylic acetoacetate with the calculated amount of the aldehyde, and then after cooling in a freezing mixture, saturating the whole with hydrogen chloride. After standing for about two days, the reaction is complete, the resulting product, *e. g.*, in the case of the condensation of ethylic acetoacetate with benzaldehyde, consisting of a mixture of two isomeric ethylic acetylbenzylchloracetates,

$$\begin{matrix} C_6H_5.CHCl \\ CH_3.CO \end{matrix}\!\!>\!\!CH.COOC_2H_5 \text{ and } \begin{matrix} C_6H_5.CH_2 \\ CH_3.CO \end{matrix}\!\!>\!\!CCl.COOC_2H_5,$$
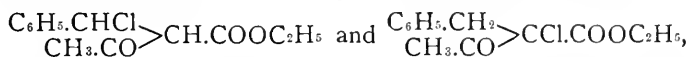
which are easily separated by crystallisation from light petroleum. Both these compounds are decomposed by distillation, yielding hydrogen chloride and ethylic acetylbenzalacetate,

$$\begin{matrix} C_6H_5.CH \\ C_6H_3.CO \end{matrix}\!\!>\!\!C.COOC_2H_5.$$

Claisen explains this condensation by supposing that the aldehyde is first converted by the hydrochloric acid into an unstable chlorhydrol, $R.CH(OH)Cl$, which then acts on the ethylic acetoacetate in the following way :

$$R.HC\!<^{OH}_{Cl} + H_2C\!<^{CCO.CH_3}_{COO_2H_5} = R.CHCl.HC\!<^{CO.CH_3}_{COOC_2H_5} + H_2O.$$
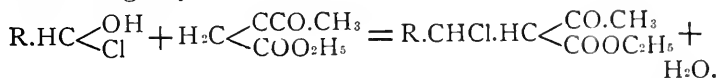
On substituting benzoylacetate for ethylic acetoacetate, it was found that condensation with aldehydes took place in precisely the

[1] Claisen, Annalen **218**, 170.

Perkin.

same way. As it appeared interesting to prove the analogy between ethylic benzoylacetate and acetoacetate in this respect also, the condensation of the former with benzaldehyde was further studied.

10 grams of ethylic benzoylacetate were mixed with 5 grams of benzaldehyde, and the whole, after being cooled below 0° in a freezing mixture, was completely saturated with hydrogen chloride. The product soon became very thick and milky, from the formation of minute globules of water, which, after standing for 24 hours at the ordinary temperature, settled out in large drops on the side of the vessel.

The dark brown oily product was dissolved in ether, well washed, first with water and then with sodic carbonate solution, to remove the excess of hydrochloric acid, and finally dried over potassic carbonate. After filtering and distilling off the ether, a dark brownish very thick oil remained ; this was distilled as rapidly as possible under diminished pressure (200 mm.), only a small residue being left. The distillate, which was nearly colorless, was distilled again, under the same pressure, the first portions, consisting of acetophenone and unchanged benzaldehyde, being rejected ; afterwards a thick oil came over, which rapidly solidified on standing. The latter was dissolved in hot methyl alcohol, from which on cooling it crystallised in beautiful colorless needles, easily obtained pure by recrystallisation.

The analysis of the crystals, dried at 70-80°, gave the following numbers:

I. 0.2243 gram of substance gave 0.1195 gram H_2O and 0.6321 gram CO_2.

II. 0.2022 gram of substance gave 0.1040 gram H_2O and 0.5665 gram CO_2.

	Found.		Theory.
	I.	II.	$C_6H_5.CO.C{<}^{CH.C_6H_5}_{COOC_2H_5}$.
C	76.86	76.83 per cent.	77.14 per cent.
H	5.91	5.74	5.72
O	17.23	17.43	17.14

The compound is therefore ethylic benzalbenzoylacetate. Ethylic benzalbenzoylacetate crystallises from methyl alcohol in long colorless glittering prisms, which melt at 98–99°. It is pretty easily soluble in hot methyl alcohol, sparingly so in cold. Like ethylic acetylbenzalacetate, it crystallises very readily. It

separates from a mixture of benzene and light pretroleum in flat plates, which polarise light splendidly. It crystallises best, however, from ether. If the ethereal solution is allowed to evaporate slowly, the sides and bottom of the vessel containing it become covered with large transparent glittering prisms, which do not lose their lustre on drying. Professor Haushofer, who kindly measured some of the crystals, gave me the following description of them:

Crystalline system monoclinic:

$$a : b : c = 1.2730 : 1 : 0.7461. \quad \beta = 86° 36'.$$

Pale yellow lustrous crystals, forming the combinations $\infty P \infty (a)$, $\infty P(p)$, $- P \infty(r)$, $P \infty (s)$, extended in the direction of the ortho-

diagonal, often also tabular on the surface a. The surfaces of this zone are smooth, but as a rule indented, and the measurements are therefore somewhat irregular.
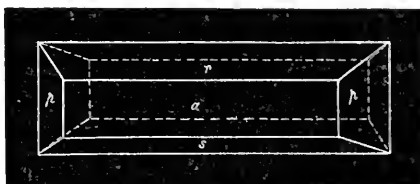
	Measured.	Calculated.
$p : p =$	103° 36′	...
$r : p =$	190 37	...
$s : r =$	119 20	...
$r : a =$	122 57	122° 53′
$p : a =$	128 .30	128 12
$s : a =$	117 53	117 47
$s : p =$	106 40	106 45

Ethylic benzalbenzoylacetate dissolves in sulphuric acid, producing a yellow solution, which, however, becomes colorless again on standing or gently warming. The solution of this body in chloroform is only very slowly attacked by bromine.

Several saponification experiments were next made, in the hope of obtaining benzylideneacetophenone, according to the equation,

$$C_6H_5.CH : C\begin{matrix}CO.C_6H_3\\COOC_2H_5\end{matrix} + H_2O =$$
$$C_6H_5.CH : CH.CO.C_6H_5 + CO_2 + C_2H_5.OH.$$
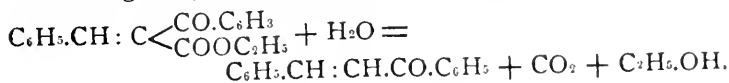
but without result. When ethylic benzalbenzoylacetate was heated with dilute hydrochloric acid in a sealed tube at 160° for seven hours, it was decomposed in part, producing a yellow oil. On opening the tube, large quantities of carbonic anhydride escaped, and on fractioning the product a considerable amount was obtained boiling below 210°, and consisting of a mixture of benzaldehyde and acetophenone. The thermometer was then removed, and the residue distilled in a vacuum, when a thick oil came over, which solidified on cooling. After crystallisation from methyl alcohol it melted at 98°, and showed all the properties of ethylic benzalbenzoylacetate. Negative results were also obtained on boiling it with potash, only small quantities of benzoic acid being produced.

Claisen[1] obtained similar results on trying to obtain ethylidene-acetone and crotonic acid by saponifying ethylic acetylethylidene-acetate, $\dfrac{CH_3.CH}{CH_3.CO}{>}C.COOC_2H_5$, with potash, and attributes this to the fact of the latter class of bodies being so easily decomposed into their components, and thus giving only aldehyde and the decomposition-products of ethylic acetoacetate, respectively ethylic benzoylacetate on hydrolysis. Another method employed by Claisen to effect the condensation of aldehydes with ethylic aceto-acetate was by heating a mixture of the two bodies in a sealed tube with acetic anhydride. In order to see whether this also took place in the case of ethylic benzoylacetate, 10 grams of the latter, 5 grams of benzaldehyde, and an excess of acetic anhydride, were heated together in a sealed tube at 180–200° for six hours. On opening the tube a large quantity of carbonic anhydride escaped. The product, which was a dark brown oil, was then directly fractioned. Below 100° a small quantity of a limpid oil came over, which, after washing and refractioning, distilled almost entirely between 70° and 80° as a light oil, smelling strongly of ethylic acetate. After the excess of acetic anhydride and acetic acid had distilled over, the thermometer rose rapidly to 180°, and between that and 210° a considerable quantity of a mixture of benzaldehyde and acetophenone came over. The residue was then distilled under diminished pressure, when the latter portions, which were collected separately, partially solidified on cooling. The crystals were first roughly freed from oily matter by spreading them out on a porous plate, and then purified by crystallisa-tion, once from methyl alcohol and once from ether.

The analysis gave the following numbers:

0.1863 gram substance gave 0.0976 gram H_2O and 0.5254 gram CO_2.

	Found.	Theory. $C_6H_5.CO$ $C_6H_5.CH$$>C.COOC_2H_5.$
C	76.92 per cent.	77.14 per cent.
H	5.82	5.72
O	17.26	17.14

The crystals melted at 98°, and the body was therefore ethylic benzalbenzoylacetate. The yield by this method was not nearly so good as by the one previously described. It is possible that the temperature employed (180-200°) was too high, and that some of the product was again resolved into its components, the ethylic benzoylacetate being further decomposed into acetophenone and carbonic anhydride.

ON RESACETOPHENONE.

By Arthur Michael and George M. Palmer.

Nencki and Sieber[1] have obtained a series of compounds by the action of anhydrous zinc chloride on mixtures of acetic acid and polyatomic phenols, which they considered as hydroxyl derivatives of acetophenone. The evidence in favor of this view is not very conclusive, as they found that resacetophenone — $C_6H_3 - \overset{(OH)_2}{CO - CH_3}$ — forms but a mono-acetyl derivative. This compound could be boiled for a long time with acetic anhydride without undergoing any change. Although the discoverers remarked that this result is somewhat surprising in view of the constitution they assigned to the compound, they have not given any further experimental support to it. It seemed to us that the formation, if correct, of but a mono-acetyl derivative makes it probable that only one hydroxyl exists in resacetophenone, as the above method is used by general consent to ascertain the number of hydroxyls in a compound, and no instance is known to us where the reagent has failed to replace all the hydrogen of the hydroxyl of alcohol radicles. One of us[2] has suggested the constitution $C_6H_4 \overset{O}{\underset{O}{}} C(OH)CH_3$,

[1] Journal für pr. Chemie [N. F.] **23**, 147.   [2] A. Michael, this Journal, 1883, 94.

which is certainly more in conformity with the formation of a mono-acetyl derivative. The following experiments were made with a view of ascertaining which of these two constitutional formulæ is correct. E. Fischer has shown that phenylhydrazine acts on ketones and aldehydes with the elimination of water, and that the reagent may be used to characterise these classes of compounds. For the purpose of ascertaining whether resacetophenone contains a carbonyl, an alcoholic solution of that substance and phenylhydrazine was allowed to stand for a day, and then the alcohol driven off. The crystalline compound that remained was purified by crystallisation from xylene and analysed with the following result:

0.4655 gram of substance gave 50.5 cc. of N, at 26.5°, and 762 mm.

$$\text{Theory for } C_6H_3 \begin{matrix} (OH)_2 \\ C-CH_3 \\ N_2HC_6H_5 \end{matrix} \qquad \text{Found.}$$

		Found.
N	11.6	12.1

The compound forms large prismatic plates that melt at 159°. It is insoluble in hot water, soluble in hot alcohol and benzene.

This result is evidently strong evidence of the presence of carbonyl in resacetophenone, and therefore that the constitution suggested by Nencki and Sieber is correct. We deemed it desirable, however, to confirm Nencki and Sieber's results on the action of acetic anhydride on resacetophenone.

A solution of twenty grams of resacetophenone in sixty grams of anhydride was heated to simmering for one hour and then fractionated. As soon as the anhydride had passed over the thermometer rose rapidly to 303°, at which temperature the acetyl-compound passed over. The crystalline distillate was crystallised several times from absolute alcohol. On analysis the following results were obtained:

0.3610 gram of substance gave 0.8210 gram of CO_2 and 0.1655 gram of H_2O.

0.3601 gram of substance gave 0.8175 gram of CO_2 and 0.1648 gram of H_2O.

	Theory for $C_6H_3\,\begin{matrix}OOCCH_3\\OH\\COCH_3\end{matrix}$	Theory for $C_6H_3\,\begin{matrix}OOCCH_3\\OOCCH_3\\COCH_3\end{matrix}$	I.	Found. II.	Nencki & Sieber.
C	61.85	61.06	62.0	61.9	61.61
H	5.15	5.08	5.1	5.08	5.38

Our compound agreed in its properties with those given by Nencki and Sieber, except that it melted at 74° instead of at

72°. These results confirm those of Nencki and Sieber that an excess of acetic anhydride only forms the mono-acetyl derivative of resacetophenone, and that the compound shows an anomalous behavior in this respect. We endeavored to obtain the diacetyl-compound by heating the compound with a mixture of anhydride and dry sodium acetate, as Lieberman has shown that this mixture always forms the highest possible acetyl derivative, but did not obtain products that could be brought into a state suitable for analysis.

Nencki and Sieber[1] mention that their attempts to obtain a hydroxyacetophenone by the action of zinc chloride on a mixture of phenol and acetic acid were without success. We have succeeded, by increasing the proportion of zinc chloride, in obtaining the compound.

Twenty grams of phenol, thirty grams of glacial acetic acid and thirty grams of zinc chloride were heated for about an hour to incipient boiling, and the product then thrown into water. The mixture was boiled until the excess of phenol was expelled ; and, on cooling, long needles were deposited on the bottom of the beaker, and some were also contained in the resin that floated on the water. They were separated as far as possible and then crystallised several times from moderately strong chlorhydric acid, by which process they were freed from zinc chloride. The crystals before treating with chlorhydric acid contained a considerable percentage of zinc, and were probably a double compound of the phenol with zinc chloride. For analysis the substance was crystallised several times from dilute alcohol.

0.2645 gram of substance gave 0.6814 gram of CO_2 and 0.1381 gram of H_2O.

	Theory for $C_6H_4<^{OH}_{CO}-CH_3$.	Found.
C	70.6	70.3
H	5.8	5.79

The compound crystallises in long prismatic needles, resembling those of phthalic anhydride, or short prisms melting at 108°. It is insoluble in hot water, but soluble in hot chlorhydric acid, separating out of the solution as it cools. In alcohol it is quite soluble. The yield obtained was very small, as the decomposition appears to proceed further with the formation of a resinous substance.

TUFTS COLLEGE, MASS.

[1] Journal für pr. Chemie (N. F.) 23, 346.

ON INACTIVE ASPARTIC ACID.

By Arthur Michael and John F. Wing.

At the time when Dessaignes[1] discovered the artificial formation of inactive aspartic acid from ammonium malate the first compound was considered as the acid amide of the other; and its synthesis, although of considerable interest, was in accordance with the general reaction of amide-formation from ammonium salts of organic acids by heating. The reaction became of far greater interest when Kolbe interpreted aspartic acid as amidosuccinic acid, as it then showed itself to be without precedent. There is no doubt that the formation of aspartic acid from ammonium malate is preceded by the elimination of water, forming either malate or fumarate, as Dessaignes[2] has shown that it may be obtained from the product formed by the action of heat on either of these compounds. The further stage of the reaction is probably very complicated, and it is an unsettled question whether the amorphous product which yields aspartic acid on continued treatment with boiling chlorhydric acid, is identical with the product obtained in the action of heat on asparagine. Artificial aspartic acid, as is well known, differs in its properties very considerably from those of the natural acid. Not only is it optically inactive, but it differs also in its crystalline form, its solubility in water; and, also, several of its salts have an entirely different form from those of the natural acid.

Such differences in properties between optically active and inactive isomers are not uncommon, although those between the compounds in question are unusually large, sufficient to make us closely examine the reasons for accepting Dessaignes' compound as amidosuccinic acid. This view rests altogether on the basic properties of the compound and its conversion by Pasteur[3] into optically inactive malic acid, but neither of these reasons can be considered as offering conclusive evidence for its constitution, especially in view of the peculiar formation of the compound.

We have endeavored to prove the constitution of inactive aspartic acid indirectly; that is, to convert the active acid into the inactive form and compare the product thus obtained with Dessaignes' compound.

[1] Compt. Rendus **30**, 324; **31**, 432.   [2] *loc. cit.*   [3] Ann. chim. phys. [3], **34**, 30.

It was found that this result was best attained by heating a dilute chlorhydric acid solution of the natural acid in closed tubes. At 100° it was found that continued heating for several days failed to cause the acid to lose its optically active properties: equally fruitless was it to heat the tubes under 160°, but heating at 170–180° for several hours sufficed to change the acid completely into the optically inactive modification. It is necessary to keep pretty closely within these limits of temperature, as at 200° the acid undergoes a complex decomposition and the contents of the tubes became quite dark in color. The contents of the tubes that had been heated to 170–180° were evaporated to dryness on a water-bath, and the acid separated according to the method given by Dessaignes. An analysis of the acid gave the following numbers:

0.269 gram of acid gave 0.3575 gram of CO_2 and 0.1283 gram of H_2O.

	Theory for $C_2H_3NH_2(COOH)_2$.	Found.
C	36.09	36.21
H	5.26	5.40

This acid agrees in all its properties with the acid obtained by treating the compound from ammonium malate with boiling nitric acid. Like that acid it crystallises in small monoclinic needles. A comparison of solubilities of this inactive acid and Dessaignes' acid gave further proof of the identity of the two products. The results, obtained by the method of V. Meyer, were as follows:

				Inactive aspartic acid by heat.	Inactive acid from ammonium malate.
At 7° C.	one part acid soluble in 238 pts. H_2O				235.9 pts. H_2O
At 5°	"	"	"	224.5 " " "	223.8 " " "
At 7°	"	"	"	238 " " "	236 " " "

The hydrochloric acid salt of the natural acid crystallises in rhombic plates, while the same salt of Dessaignes' acid crystallises in monoclinic prisms. It was found that the salt of the natural acid rendered inactive also crystallises in similar monoclinic crystals. A further difference exists between the crystalline forms of the sodium salts, that of the active acid belonging to the rhombic, and the salt of Dessaignes' acid to the monoclinic. In this case, also, the identity of the inactive acids showed itself. We believe that these results show quite conclusively that Dessaignes' acid is really amidosuccinic acid; in fact, the optically inactive modification of the natural acid. In regard to its formation from acid

ammonium malate, it may be supposed that the acid amide of fumaric or maleic acid is formed as the first stage of the reaction,[1] and that this compound passes over into the lactimide of aspartic acid, or some derivative of it formed by elimination of water; a reaction which would be somewhat similar to the formation of the lactone of β-oxycarboxylhydrocinnamic acid from carboxylcinnamic acid by heating:

$$
\begin{array}{ll}
\begin{array}{l}
\text{CH}-\text{CONH}_2 \\
\quad | \\
\text{CH}-\text{COOH}
\end{array}
&
\begin{array}{l}
\qquad\quad \text{NH} \\
\text{CH}<\quad | \\
= | \quad\ \text{CO} \\
\text{CH}_2-\text{COOH}
\end{array}
\\[2em]
\begin{array}{l}
\qquad \text{CHCHCOOH} \\
\text{C}_6\text{H}_4 \\
\qquad \text{COOH}
\end{array}
&
= \text{C}_6\text{H}_4{\text{CH}\atop \text{CO}}{<}{\text{CH}_2.\text{COOH}\atop \text{O}}
\end{array}
$$
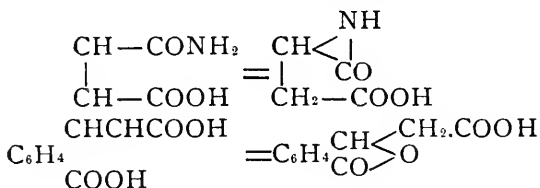
We have attempted to prove the formation of amido acids by heating the acid ammonium salts of unsaturated polybasic acids, but without obtaining any success. Neither from ammonium citraconate, mesaconate, nor tricarbyllate could a basic product be obtained.

It seemed possible that by heating acid aniline malate, and treating the condensation-product with mineral acids, phenylamidosuccinic acid, or a quinoline derivative, might be obtained, and for this reason the experiment was made. Malic acid and aniline, in the proportion of equal molecules, were heated in a water-bath for several hours, then brought into a retort and heated gradually in a paraffine bath up to 230–250°. At first water was driven off, then long yellow needles sublimed into the neck of the retort, and a dark-colored residue remained behind. The yellow sublimate was purified by several crystallisations from water, and gave the following results on analysis:

0.2872 gram of substance gave 0.7642 gram of CO_2 and 0.1262 gram of H_2O.

0.1484 gram of substance gave 18 cc. of nitrogen at 21° and 750 mm.

	Theory for $C_2H_2{\text{CONHC}_6\text{H}_5 \atop \text{CONHC}_6\text{H}_5}$	Found.
C	72.10	72.55
H	5.26	4.86
N	9.86	10.19

The substance crystallises from water as slender yellow needles, often three or four inches in length. It melts at 87°.5.

[1] The compound formed by heating acid ammonium malate is still called fumarimide. This name should disappear, as the compound evidently is not a derivative of fumaric acid.

By continued boiling with water it decomposes into fumaric acid and aniline, a decomposition that proceeds much faster when it is boiled with chlorhydric acid. The substance is evidently the anilide of fumaric acid.

The dark residue remaining in the retort was insoluble in water; soluble with difficulty in alcohol. It was soluble in alkalis, and after the solution has been heated acid gave a precipitate which proved to be fumaric acid. No basic compound other than aniline could be isolated from it.

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REVIEW.

LEHRBUCH DER ALLGEMEINEN CHEMIE.   Erster Band: Stöchiometrie.
    Von DR. WILH. OSTWALD, Professor am Polytechnikum zu Riga.

This book furnishes fresh evidence of the increased attention which the subject commonly called physical chemistry is attracting. The object of the book is to present in an orderly way the results which have been reached in investigating chemical action as such. It is not a treatise on chemical substances, but it has reference to the way in which chemical substances act upon one another, and to the fundamental hypotheses of the science of chemistry. The first volume deals with the subject of stoichiometry in its broadest sense, everything of importance that has any connection with the problem of determining atomic weights being discussed.

In the second chapter the results of the author's own recalculations of the atomic weights are given. In discussing these results he, of course, gives a passing consideration to Prout's hypothesis, and rather summarily disposes of it in these words: "Stas's results having been shown to be correct, the fate of Prout's hypothesis in its original form is finally decided—it is false."

The second book is entitled "Stöchiometrie gasförmiger Stoffe." Under this head are treated the phenomena of gases, so far as these are of importance in connection with the subject of atomic weights. The law of Gay Lussac and the hypothesis of Avogadro, the kinetic theory of gases, the specific heat of gases, and the optical properties of gases are the subjects of the chapters which make up the second book.

The third book is entitled "Stöchiometrie der Flüssigkeiten." This includes such subjects as volume relations of liquid substances,

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solutions, refraction of light by liquids, rotation of the plane of polarisation, capillarity, diffusion and osmose, and the specific heat of liquids.

Under the head of " Stöchiometrie fester Körper,' which is the title of the fourth book, the following subjects are taken up : the general properties of solid bodies, volumes of solid bodies, crystals, isomorphism and polymorphism, optical properties of solid bodies, changes in the state of aggregation, specific heat and adsorption.

Finally, in the fifth and last book of the first volume, the general subject " Systematik " is treated. The special subjects are : the choice of atomic weights, the periodic law, the molecular theory, and the theory of chemical compounds.

The book is characterised by great clearness, and the recognition of the boundary between the region of facts and that of hypothesis. In his preface the author says : " In preparing my book I have constantly kept in mind the necessity of carefully separating the observed facts from hypotheses and theories. To the former I have given their fullest value, the latter I have properly represented as the result of experience and limited by it.

" I may perhaps hope that by so doing I have rendered a service at this time, when the accusation is made against the present direction of chemistry, and frequently with justice, that hypotheses are confused with facts."

Of the periodic law the author speaks very highly. He considers that the recognition that the properties of the elements are periodic functions of their atomic weights, is one of the most important advances made in the science of chemistry in recent times. Every attempt to find similar comprehensive regularities when other atomic weights were used than those now commonly accepted has been a complete failure, so that the periodic law deserves to rank with isomorphism, and with the law of Dulong and Petit and of Avogadro, as furnishing a reliable means of determining atomic weights.

There is no book which gives a more satisfactory treatment of the subjects taken up than this does. Its careful study cannot fail to aid the student to think clearly and to secure a firm foundation for his thoughts.   I. R.

AMERICAN

CHEMICAL JOURNAL.

THE SEPARATION OF TITANIUM AND ALUMINUM, WITH A NOTE ON THE SEPARATION OF TITANIUM AND IRON.[1]

BY F. A. GOOCH.

In attempting to separate titanium and aluminum it is usual to resort to that method which depends upon the action of the slightly acid solution of the sulphates when submitted to prolonged boiling. The faultiness of this method, however, becomes apparent when solutions of aluminum and titanium are compared as to behavior under the conditions. To secure the complete precipitation of titanium the excess of sulphuric acid must be kept small, while to prevent the deposition of alumina the acid must be more than enough to dissolve the same amount freshly precipitated as hydrate, in the cold. Thus, upon boiling solutions containing the equivalent of 0.06 gram of titanic oxide, 2.5 grams of free sulphuric acid, beside alkaline sulphates, in 800 cm.[3] of water, it was found that at the end of an hour 0.003 gram of titanic oxide in one case, and 0.006 gram in another experiment, had escaped precipitation; but that, when the solution of titanium had first been precipitated by ammonia and then made just acid by sulphuric acid, every trace of dissolved titanium was thrown out on boiling. The experiment, on the other hand, of boiling a gram of alum—roughly speaking 0.1 gram of alumina—in 800 cm.[3] of water shows almost immediately the deposition of some alumina,

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[1] Communicated by the Author, from the Proceedings of the American Academy of Arts and Sciences.

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and the same thing happens when the alumina is first precipitated by ammonia and then dissolved by just enough sulphuric acid to effect the solution. The difficulty of so adjusting the acidity of the solution that no alumina shall be deposited and no titanium held up, is obvious. Test paper is of no aid in the case, since the reaction of alum itself and aluminic sulphate is acid. Under the circumstances it is hardly surprising that Knop[1] should revert from the troublesome, and only under remote conditions more exact, method of separation by boiling, to the convenient but indubitably inaccurate process of parting by the use of sodic hydrate. Knop employs both the dry and the wet method,—the fusion of the oxides in sodic hydrate, and the treatment of the salts in solution with sodic hydrate in excess; but both had long before been generally discarded, and the single experiment of acidulating the alkaline filtrate from a precipitate obtained by the treatment of a pure titanium salt according to either mode, and then making alkaline with ammonia, is enough to prove their worthlessness.

In an endeavor to secure a better means of separating titanium from aluminum I have followed two lines of experimentation; the one based upon the observation that, under properly controlled conditions, titanium is completely precipitated and alumina held in solution when an alkaline orthophosphate, strongly acidified with formic acid, is added to the solution of salts of these elements; the other, upon the solubility of alumina and the insolubility of titanic hydrate in sufficiently strong boiling solutions of acetic acid. Two preparations of titanium were used as test material in the course of the work; the solution of the fusion in sodic bisulphate of the hydrate precipitated by ammonia from the fluoride of titanium and potassium itself made from rutile and carefully purified by recrystallisation; and the solution obtained by treating the carefully prepared double fluoride with sulphuric acid, evaporating to dryness, redissolving in sulphuric acid and diluting with water. The second mode of preparation is the better, because the amount of alkaline sulphate present in the test solution is much smaller. At first, the strength of the solution was fixed by precipitating weighed amounts by ammonia, carefully washing, igniting and weighing the precipitate; but in the course of the work it became plain that the precipitation by means of ammonic acetate, or by ammonia with the

subsequent addition of acetic acid in distinct excess, yielded more precise results. On this account, therefore, the determinations of the standard of the solutions employed in the later work were made by the acetic acid process, and the determinations by ammonia were corrected to correspond. In some of the experiments bearing upon this point, the results of which are given in the figures below, precipitations by ammonia were made in the cold and the liquid then heated to boiling ; in those in which acetic acid was used just in excess, this reagent succeeded the ammonia at once, and the boiling followed ; when precipitation was effected in presence of large amounts of acetic or formic acid, the acid was added in the amount intended, sodic acetate in quantity more than that necessary to decompose the sulphates present was introduced, and the clear solution heated to boiling, and kept boiling for a minute or two. The acetic acid employed was the C. P. article of commerce, and contained thirty-five per cent. of absolute acid. The amounts of it used—20 per cent., 30 per cent., 40 per cent., 50 per cent. by volume—correspond to 7 per cent., 10.5 per cent., 14 per cent., 17.5 per cent. of absolute acid. The formic acid contained twenty-seven per cent. of pure acid, and when it is said that there was in solution 5.4 per cent. of it, the absolute acid is meant ; but it was the weaker acid, to the amount of 20 per cent. of the entire volume, which was actually used. The experiments were made in sets, and so appear in the record, in consequence of changes (due to slight depositions from time to time) in the strength of the test solution, which necessitated redeterminations of standard.

	Weight of Solution.	TiO$_2$ found.	TiO$_2$ in 50 grams.	Mode of Precipitation.
(1)	52.7370 grams.	0.3177 gram.	0.3012 gram.	} By ammonia.
(2)	52.7610	0.3180	0.3012	
(3)	52.7620	0.3076	0.2912	} By ammonia and ex-
(4)	41.8010	0.2436	0.2914	cess of acetic acid.
(5)	52.9420	0.3381	0.3193	} By ammonia.
(6)	53.0200	0.3384	0.3191	
(7)	10.6300	0.0667	0.3137	} By acetic acid 7 per
(8)	10.6960	0.0671	0.3137	cent. by volume.
(9)	21.1030	0.1285	0.3044	} By ammonia.
(10)	21.1480	0.1290	0.3049	
(11)	21.0810	0.1248	0.2960	} By acetic acid 14 per
(12)	21.1670	0.1259	0.2974	cent. by volume.

	Weight of Solution.	TiO$_2$ found.	TiO$_2$ in 50 grams.	Mode of Precipitation.
(13)	21.0620 grams.	0.1270 gram.	0.3015 gram.	} By ammonia.
(14)	21.2310	0.1279	0.3012	
(15)	10.4370	0.0617	0.2956	} By acetic acid 10.5
(16)	10.6590	0.0629	0.2950	per cent. by volume.
(17)	10.4870	0.0618	0.2946	} By acetic acid 14 per
(18)	10.8820	0.0637	0.2940	cent. by volume.
(19)	10.4700	0.0615	0.2938	} By formic acid 5.4
(20)	10.7410	0.0627	0.2919	per cent. by volume.
(21)	52.3960	0.3396	0.3230	} By ammonia.
(22)	52.4140	0.3378	0.3222	
(23)	52.6350	0.3340	0.3262	
(24)	52.5600	0.3372	0.3208	} By acetic acid in dis-
(25)	52.4830	{ 0.3366$_1$ 0.3363$_2$	0.3207 0.3204	tinct excess.
(26)	52.3700	0.3348	0.3196	} By acetic acid 17.5
(27)	52.6420	0.3374	0.3205	per cent. by volume.

It will be noticed in the examination of these figures that parallel determinations usually agree very closely. The amounts of titanic oxide indicated by those experiments in which the precipitation was made by ammonia, are much in excess of those in which acetic acid was added subsequently. Thus the difference between (1), (2) and (3), (4) amounts to more than three per cent. of the total amount of the former; that between (5), (6) and (7), (8), to a little less than two per cent.; that between (9), (10) and (11), (12), to about two and a half per cent.; and a correction of more than two per cent. must be applied to (13), (14) to bring them to correspondence with (15), (16), (17), (18). The difference between (21), (22), (23) and (24), (25), (26), (27) is about one per cent., and the smallness of this figure in comparison with the differences previously noted is apparently explicable by the fact that the solution of titanium employed in the last determinations was prepared by the second of the methods mentioned above, and carries a smaller amount of alkaline sulphate. The tendency of titanic hydrate to include the sulphates of the alkalies is not strange in view of the well-known conduct of aluminic hydrate under similar circumstances, but the amount thus held is rather surprising. The experiments in which different proportions of free acid were introduced go to show, very strikingly, that, if acetic acid exerts any solvent action whatever upon the precipitate

thrown down by boiling the acetate, that action is very slight. Thus, between the mean of (24), (25) and that of (26), (27)—the one set precipitated by ammonia and treated before boiling with just a distinct excess of acetic acid, the other pair thrown out of a large volume, 700 cm.³, one-half of which was acid of 35 per cent. strength, by boiling—we find a difference of but 0.0007 gram, and between the mean of (15), (16) and that of (17), (18), the difference (magnified five times by reference to 50 gram portions) is 0.0010 gram. In (25), too, we have an experiment in which the weighed precipitate was fused in sodic carbonate, dissolved, and again precipitated as before and weighed, the two weights differing by 0.0003 gram. Moreover, the filtrates from the precipitates thrown out in presence of an excess of acetic acid, when neutralised with ammonia, failed invariably to show the smallest precipitate, and in direct experiments upon the sensitiveness of the reaction it was found that on the addition of 0.0005 gram of titanic oxide in solution to 100 cm.³ of 35 per cent. acetic acid carrying a little sodic acetate, a distinct precipitate appeared almost immediately on boiling. It is plain, therefore, that so far as concerns the purpose in hand, the insolubility of the titanium precipitate in acetic acid may be taken as absolute. The small apparent losses to be observed in some of the determinations in which a large excess of acetic or formic acid was employed, are probably explicable by the tendency of the precipitate to change its consistency as the amount of free acid increases, and, in very acid solutions, to show an inclination to adhere in small amounts, but quite persistently, to the vessel in which precipitation takes place. The adherent precipitate may be dislodged with ease by putting a little hydrochloric acid into the beaker to which the precipitate adheres, covering and heating gently so that the acid volatilised may condense upon the walls of the beaker and again run down. By then rubbing the walls of the beaker a little and adding ammonia in excess, the trace of residual titanium is completely recovered. This method of recovery was applied in (26) and (27).

In preliminary experiments upon the first of the methods which seemed to promise a separation of titanium and aluminum, it was found that the precipitation of titanium by an alkaline orthophosphate is complete in the presence of a large amount of acetic or formic acid, and that, in the cold, and under conditions otherwise properly controlled, aluminic phosphate fails to appear. To

hold up the alumina by means of acetic acid requires some care in
the adjustment of the acid and phosphate, and to redissolve the
precipitate once formed is a matter of considerable difficulty.
Thus, to clear the solution of a precipitate produced by 1.5 grams
of the phosphate of soda and ammonia upon 0.1 gram of alumina,
it was necessary to dilute the liquid to a volume of 250 cm.³, and
add acetic acid until there was in the solution at least five per cent.
of absolute acid ; and the addition of 1.5 grams more of the precipi-
tant again precipitated aluminic phosphate. Formic acid, how-
ever, is more active, and the balance between it and the precipitant
not so delicate. When the proportion of three parts by weight of
absolute formic acid to two parts of microcosmic salt is kept, the
aluminic phosphate does not fall ; and if, because of a deficiency
of acid, precipitation does not take place, the liquid immediately
clears so soon as the proportion of acid and precipitant is restored.
Formic acid, therefore, was used in the experiments about to be
described. The test solution of titanium was that employed in the
previous experiments (1) to (20), but, inasmuch as the error of the
process had not yet been remarked, the standards were determined
by precipitating by ammonia, and are therefore to be corrected.
The application of a correction of two and a half per cent. to the
apparent weights of titanic oxide found by the ammonia process
—the mean correction for (1), (2), (5), (6), (9), (10), (13), (14)—
cannot lead far away from the truth, since the difference between
the maximum and minimum corrections observed amounts for the
quantity of material employed in these experiments to but 0.0002
gram. Determinations of standard, original and corrected, are
given in (28), (29), (30), and (31).

	Weight of Solution.	TiO_2 found.	Corrected TiO_2 in 50 grams.	Corrected TiO_2 in 50 cm.³
(28)	52.7660 grams.	0.3867 gram.	0.3572 gram. ⎫	0.3771 gram.
(29)	52.8410	0.3869	0.3569 ⎭	
(30)	52.5380	0.3810	0.3627	
(31)	52.6920	0.3822	0.3627	

A portion of the solution, the standard of which is set by (28)
and (29), was diluted to ten times its volume, and 50 cm.³ of the
diluted solution were used in each of the experiments immediately
following. These were made to determine whether the precipitate
was definite in composition, and might be weighed as such. Pre-
cipitation was effected by a solution of microcosmic salt acidified
with formic acid. The precipitates of (32) and (33) were collected

on paper, that of (34) on asbestos, and all were ignited and weighed directly.

	Amount taken.	TiO_2 and P_2O_5 found.	TiO_2 by Standard.	P_2O_5 by Difference.
(32)	50 cm.[3]	0.0731 gram.	0.0377 gram.	0.0354 gram.
(33)	"	0.0640	0.0377	0.0263
(34)	"	0.0753	0.0377	c.0376

The phosphate obtained by Merz[1] by precipitating in presence of hydrochloric acid containing two molecules of TiO_2 to one of P_2O_5, requires 0.0326 gram of P_2O_5 to 0.0377 gram of TiO_2. It will be noticed that in two determinations the P_2O_5 is in a considerable excess of the amount demanded by this proportion, and in one, in deficiency. The idea of weighing the phosphoric anhydride and titanic oxide together was therefore abandoned.

In experiments (35), (36), (37), the titanium was present alone; in (38), (39), 2 grams of alum were added to the solution before precipitating by means of the mixture of microcosmic salt and formic acid, 5 grams of the former being employed to 8 grams of the latter. The precipitates of all, excepting (35), were carefully washed, ignited, fused with sodic carbonate, and the product of fusion was dissolved in water, the insoluble titanate separated from the soluble phosphate by filtration and washing, ignited, again fused with a little sodic carbonate, the result of fusion dissolved in strong sulphuric acid, diluted with water, and precipitated by ammonia with the subsequent addition of acetic acid, and boiling. Experiment (35) was conducted in like manner, excepting that the sodic titanate was dissolved off the filter by means of a mixture of hydrochloric and oxalic acids, the latter destroyed by potassic permanganate (since there is danger that in presence of ammonic oxalate the titanium may not be completely precipitated by ammonia), ammonia added in excess, then acetic acid to strongly acid reaction, and the liquid boiled. This mode of treating the acid titanate is not desirable, since the titanic hydrate, if precipitated but once subsequently, retains a trace of manganese. To fuse the titanate with sodic carbonate, and then treat the melt with strong sulphuric acid, is probably the best way of getting the titanium into solution again. The test solution of (28) and (29) was employed in experiment (35), and that of (30) and (31) in the rest.

From experiments (36) and (37), together with (35), which, as has been remarked, would naturally give figures slightly too high,

[1] Jour. prakt. Chem. **99**, 157.

it appears that the method indicates with accuracy the amount of titanium present. Experiments (38) and (39) indicate that the separation from alumina is not unreasonably inexact.

	Weight of Solution.	TiO₂ found.	TiO₂ by Standard.	Error.	
(35)	5.2220 grams.	0.0383 gram.	0.0373 gram.	0.0010 gram	+
(36)	5.2300	0.0371	0.0370	0.0001	+
(37)	5.3840	0.0380	0.0381	0.0001	—
(38)	5.2920	0.0367	0.0374	0.0007	—
(39)	5.2540	0.0383	0.0372	0.0011	+

The tediousness of filtration, which is a consequence of the nature of the phosphate precipitate, is the great objection to the method, and on account of it the testing was pushed no further, attention being turned instead to the second line of experimentation.

The incompleteness of the precipitation of alumina by the basic acetate process in presence of a large excess of acetic acid, suggested the attempt to hold up alumina entirely by means of a sufficient excess of acetic acid while precipitating titanium. Experiments to determine the amount of acetic acid necessary to prevent the precipitation of alumina from a boiling solution of the acetate, indicate that amounts of absolute acid in excess of five per cent. by volume of the solution are adequate to the purpose, and that the addition of sodic acetate in reasonable amounts does not sensibly affect conditions. It appears, further, that the addition of a very small quantity of titanium in solution to the clear boiling solution of alumina in acetic acid occasions at once a perceptible precipitation. Thus, 0.0005 gram of titanic oxide in solution produced a distinct and appreciable opalescence in 500 cm.³ of liquid containing 10 grams of alum, 15 grams of sodic acetate (about twice the amount necessary to convert the sulphate of alumina to the acetate), and seven per cent. by volume of absolute acetic acid.

In respect to holding up alumina, formic acid acts like acetic acid, but more potently.

In the following experiments to test the method quantitatively, two solutions of titanium were employed: in (40) and (41), the solution the value of which was fixed by (15) to (18); in (42) to (46), the solution whose standard was set by (24) to (27). To the cold solution of titanium containing a little free sulphuric acid together with some alkaline sulphate were added 5 grams of alum

(approximately 0.5 gram of alumina), 20 grams of sodic acetate, which was always more than enough to effect the entire conversion of the aluminic and titanic sulphates to acetates, acetic acid to such amount that in experiments (42), (43), (44) there should be in the solution seven per cent. by volume of absolute acid, and in the remaining experiments ten and a half per cent. by volume, and water to make the entire volume 250 cm.³ in (40) and (41), and 400 cm.³ in the rest. The clear solutions obtained in this manner were raised quickly to boiling, kept at that point for a minute, and removed from over the burner so that the precipitate might settle, as it does almost immediately. The supernatant liquid was decanted upon a filter sufficiently porous to permit very rapid filtration,[1] and the precipitate added immediately thereafter, and washed with 7 per cent. acetic acid followed finally by hot water. The washed precipitate was dried, ignited and weighed. The precipitate once upon the filter and drained becomes more compact and easily washed, and strong ignition of fifteen or twenty minutes over a good Bunsen burner, after the paper is thoroughly ashed, reduces it to a weight which neither the blast-lamp nor ignition in an atmosphere of ammonic carbonate changes.

	Weight of Solution.	TiO_2 found.	TiO_2 by Standard.	Error.	
(40)	10.4910 grams.	0.0645 gram.	0.0618 gram.	0.0027 gram	+
(41)	10.5970	0.0656	0.0624	0.0032	+
(42)	20.9520	0.1450	0.1343	0.0107	+
(43)	21.1750	0.1439	0.1357	0.0082	+
(44)	21.0250	0.1431	0.1347	0.0084	+
(45)	20.8740	0.1393	0.1338	0.0055	+
(46)	21.0570	0.1402	0.1349	0.0053	+

It is quite obvious that a single precipitation by the method used does not yield titanic oxide free from alumina. The weighed precipitate of each experiment was therefore fused with a small quantity of sodic carbonate, and the product of fusion treated in the crucible with strong sulphuric acid, which gradually with the aid of gentle heat dissolved everything completely. This solution after cooling was poured directly into 100 cm.³ of cold water, and, the liquid remaining clear, ammonia was added just to alkalinity, and then dilute sulphuric acid corresponding to 2.5 grams of pure

1 The paper No. 589 of Schleicher and Schull is excellent for the purpose.

acid. The precipitate thrown down by ammonia was gradually, but after a few minutes entirely redissolved, acetic acid was added until it amounted in terms of absolute acid to ten and a half per cent. of the entire volume, 20 grams of sodic acetate introduced, the solution boiled, and the precipitate treated as previously described. The results of this second treatment are given below.

	Weight of Solution.	TiO_2 found (II).	TiO_2 by Standard.	Error.	
(40)	10.4910 grams.	0.0624 gram.	0.0618 gram.	0.0006 gram	+
(41)	10.5970	0.0623	0.0624	0.0001	—
(42)	20.9520	0.1373	0.1343	0.0030	+
(43)	21.1750	0.1385	0.1357	0.0028	+
(44)	21.0250	0.1369	0.1347	0.0022	+
(45)	20.8740	0.1357	0.1338	0.0019	+
(46)	21.0570	0.1383	0.1349	0.0034	+

In experiments (40) and (41), in which comparatively small amounts of titanium were employed, the separation from alumina was reasonably good after the second precipitation, but in (42) to (46) the larger quantities of titanic oxide still retained notable amounts of alumina. The precipitates of (45) and (46) were, therefore, treated again just as before, to determine the effect of a third precipitation.

	Weight of Solution.	TiO_2 found (III).	TiO_2 by Standard.	Error.	
(45)	20.8740 grams.	0.1347 gram.	0.1338 gram.	0.0009 gram	+
(46)	21.0570	0.1360	0.1349	0.0011	+

Three precipitations left the titanic oxide of these experiments nearly free from alumina, but three such treatments involve a good deal of labor, and, moreover, it is evident that the precipitate still holds with tenacity traces of alumina. The experiment of attempting to remove residual alumina after a single precipitation, by treating the product of fusion of the precipitate in sodic carbonate with boiling water, filtering, igniting the residue, again fusing with a little sodic carbonate, and proceeding from this point to dissolve in sulphuric acid and precipitate once more as before, was therefore tried, and the result is given in the record of (47) to (50).

	Weight of Solution.	TiO_2 found.	TiO_2 by Standard.	Error.	
(47)	20.8640 grams.	0.1329 gram.	0.1337 gram.	0.0008 gram	—
(48)	21.1100	0.1345	0.1354	0.0009	—
(49)	20.9100	0.1332	0.1340	0.0008	—
(50)	21.0020	0.1348	0.1346	0.0002	+

This mode of treatment appears to remove the last traces of alumina, and yields a reasonably good separation.

It appears, therefore, to recapitulate, that for the separation of titanium and aluminum either of the processes set forth in the preceding work may serve. The first, however, which is, in brief, the treatment of the solution containing salts of the elements in question with a mixture of microcosmic salt and formic acid, in the proportion of two to three by weight, together with enough ammonic formate to take up the stronger acids, fusing the precipitate in sodic carbonate, extracting with water, fusing the residue in a small amount of sodic carbonate, dissolving in sulphuric acid and precipitating by ammonia with the subsequent addition of acetic acid, and boiling—though probably fairly accurate, is, on account of the nature of the precipitated phosphate, not comparable with the second method in point of convenience. The latter process, which involves many different manipulations—the introduction into the solution of titanium aud aluminum of enough acetic acid to make from seven to eleven per cent. by volume of the absolute acid, together with sufficient sodic acetate to fix all of the stronger acids in sodium salts, boiling, filtering and washing with acetic acid of seven per cent. strength, fusing the ignited precipitate in sodic carbonate, extracting with boiling water, again fusing the residue with a little sodic carbonate, dissolving in strong sulphuric acid and pouring this solution into water, neutralising with ammonia, redissolving the precipitate in a known amount of sulphuric acid, and precipitating finally by boiling with acetic acid and sodic acetate as at first—and appears in the description to be long and tedious, may in reality be carried out with ease and rapidity, the operations being generally short and not of a difficult nature.

In most cases in which titanium is to be separated from aluminum, it is necessary to effect the removal of iron as well. Some experiments looking to the separation of titanium and iron, by boiling the acetates in presence of a large excess of acetic acid, were unsuccessful ; for, though an excess of acetic acid amounting to eleven per cent. of absolute acid in the solution is enough to prevent the deposition of a basic ferric acetate, it appears, unexpectedly, that in presence of ferric acetate in solution the titanium shows a very marked tendency to remain dissolved. Thus, an amount of iron alum the equivalent of 0.2 gram of ferric oxide, together with 10

grams of sodic acetate and seventeen per cent. of absolute acetic
acid, in a total volume of 400 cm.[3], held 0.06 gram of titanic oxide
completely in solution during boiling prolonged a quarter of an
hour. In an experiment the counterpart of this, excepting only
the addition of sodic acetate, the titanium began to deposit at once
on boiling ; and Streit and Franz,[1] in proposing the ebullition of
the sulphates in presence of a large excess of acetic acid as a means
of procuring titanic oxide free from iron, claim a complete precipi-
tation under these conditions. The behavior of the sulphates of
titanium and zirconium when in solution together appears to be
analogous to this action of the acetates of iron and titanium, and
iron in the ferric condition is generally supposed to influence some-
what the precipitation of titanium from the solution of the sulphates.

When iron and titanium appear together in solution, and are to
be separated, the choice lies between Stromeyer's application of
Chancel's hyposulphite method,[2] which yields milky filtrates,—
always undesirable,—and that process which involves the precipi-
tation of iron by ammonic sulphide in presence of ammonic tartrate
to hold up the hydrates which would be precipitated in its absence.
This latter method has been regarded as an undesirable one, chiefly
on account of the inconvenience involved in the evaporation of the
filtrate from the ferrous sulphide and the ignition of the residue to
remove the tartaric acid, and so to permit the recovery of the
bases. The difficulty in question may be obviated, however, by
destroying the tartaric acid by potassic permanganate added
gradually to the hot solution containing enough free sulphuric
acid to leave some excess after the conversion of all the perman-
ganate. The oxidation of tartaric acid by potassic permanganate
does not, as is well known, yield carbonic acid and water alone, but
gives rise also to a considerable quantity of formic acid as an inter-
mediate product. When the permanganate begins to act upon the
formic acid, the oxidation, going more slowly, results in the depo-
sition of a brown manganic hydrate, which, if any tartaric acid
remains in solution, redissolves quite rapidly, and in presence of
formic acid as the only reducing agent, more slowly. When,
therefore, manganic hydrate is abundantly precipitated in the
boiling solution, and does not perceptibly dissolve, it is quite
certain that the conversion of the tartaric acid to formic acid—
which is all that is needed in this case—has been accomplished ;

[1] Jour. prakt. Chem. **108**, 65.   [2] Ann. Ch. Pharm. **113**, 127.

but for the sake of greater security the addition of permanganate may be continued until its color shows in the solution. It is well, however, to make use in this process of a known amount of tartaric acid,—experience has shown that an amount equal to three times the weight of the oxides to be held in solution is sufficient, unless ammonia be used in enormous excess and the boiling prolonged,— and to employ for its destruction two and a half times its own weight of potassic permanganate, this quantity being more than enough to carry the oxidation to the final products, providing there were no deposition of manganic hydrate. The manganese thus introduced into the solution may be removed by two acetate precipitations, which, if alumina is to be separated, must be made at any rate, even if no manganese be present.

To separate titanium, aluminum and iron, therefore, I find it most convenient to precipitate the iron by passing hydric sulphide into the faintly ammoniacal solution of the oxides in ammonic tartrate, taking care that the solution is still ammoniacal just before filtering ; to destroy the tartaric acid in the filtrate, after acidifying and boiling off the hydric sulphide by means of potassic permanganate in the manner just described, redissolving residual manganic hydrate by the addition of a little ammonic bisulphite, and boiling off the excess of sulphurous acid ; and to separate the titanium and aluminum by the acetate process.

A single point in the analysis of silicates may be worthy of note in this connection. If phosphoric acid be present, as is often the case, the separation of titanium from silica by the action of cold water upon the product of fusion in sodic or potassic bisulphate is liable to uncertainty, on account of the formation of the insoluble titanic phosphate which remains partly with the silica and in part clouds the filtrate. The siliceous residue should, therefore, be treated with sulphuric and hydrofluoric acids to recover titanium which may be with the silica. It is better in most cases to effect the decomposition of a silicate by means of one of the fluoride methods, or by fusion in an alkaline carbonate, the melt in the latter case being acidified with hydrochloric acid, and the residue after evaporation and filtration worked over with sulphuric and hydrofluoric acids for the recovery of that portion of the titanium which remains insoluble after the evaporation.

A NEW METHOD FOR THE DETERMINATION OF PHOSPHORUS IN IRON AND STEEL.[1]

By J. B. Mackintosh.

The general method which has been followed since the time of Heinrich Rose, and perhaps before, for the determination of phosphorus in iron and steel, is to dissolve the sample either in nitric acid, *aqua regia*, or some other oxidising agent, in order to convert the phosphorus into phosphoric acid.

In 1832 Rose[2] recommends HNO_3, or *aqua regia*, preferably the former. Wöhler, in 1854,[3] directs that the iron should be oxidised by burning in a stream of oxygen for the determination of carbon, and the resulting oxide of iron containing all the phosphorus as phosphoric acid be treated as an ore. In the fourth English edition of Fresenius' Quantitative Analysis,[4] pp. 666–667, we find directions to dissolve the iron in *aqua regia* or bromine ; and, coming down to more recent times, we find F. A. Cairns[5] directing the employment of a boiling solution of potassium chlorate and hydrochloric acid for the oxidation and solution of the sample to be analysed. It is unnecessary to multiply quotations from the literature of the subject, though they might be extended almost indefinitely, since it would only be a repetition of the above-mentioned series of methods in one form or another ; and the references given have been selected to show how little essential variation there is in the type-methods of solution used. In fact it seems to be universally accepted as a necessary first step in the determination that some such method of solution should be followed.

One chemist, however, struck out on a different line of thought, and to the best of my knowledge only one, M. V. Tantin, who, in a contribution to the Comptes Rendus (I have not been able to find the original article, however), copied in the Chemical News,[6]

[1] Communicated by the Author, from the Transactions of the American Institute of Mining Engineers.

[2] Rose's Traité Pratique d'Analyse Chimique. Translated from the second German edition, by A. J. L. Jourdan, 1832, 2, 414.

[3] Wöhler's Handbook of Inorganic Analysis. Edited by A. W. Hofmann. London, 1854, 61.

[4] 1865. [5] A Manual of Quantitative Chemical Analysis. By F. A. Cairns, A. M., 1880, 114.

[6] Chemical News 18, 252.

describes his method for determining phosphorus in cast-iron as follows:

"When seeking the means of avoiding these sources of error,[1] I concluded that the best way of so doing would be to use a precisely contrary method ; namely, by liberating the phosphorus as a hydrogen compound ; but one objection naturally arose—would the totality of the phosphorus pass into the state of a gaseous product? I may safely affirm that I have never been able to discover the least trace of phosphorus in the residue after the complete attack of the cast-iron by chlorhydric acid, which fact is not surprising if it be considered what strong affinities phosphorus has for hydrogen."

According to M. Tantin, the resulting gases, composed of phosphuretted, arsenuretted, sulphuretted, and carburetted hydrogen, are passed through potash and then into nitrate of silver, where all the phosphuretted hydrogen is caught as phosphide of silver, which is afterwards treated with *aqua regia*, and the phosphoric acid resulting determined as ammonic-magnesic phosphate. The following precautions are mentioned as indispensable.

1. The cast-iron must be attacked very slowly, or part of the phosphuretted hydrogen may traverse the solution of nitrate of silver without being absorbed.

2. When the solution is finished, a current of hydrogen is to be passed through the apparatus.

M. Tantin seems to have overlooked the possibility of some of the phosphorus remaining in the solution, and to have assumed that if none was found in the residue, all must have gone off with the gas. If such were the case, the determination of phosphorus would be much simplified.

Some years ago I tried this method on a pig-iron which I knew contained over one per cent. of phosphorus, but my final precipitate, if any, of ammonic-magnesic phosphate was so small as to be invisible. I concluded that the method was not suited for American pig-irons, and gave no more attention to the subject till the present summer, during which I have had considerable leisure time for experiment.

In Watts's Dictionary of Chemistry[2] we find the statement, "When a very small quantity of phosphorus is associated with a

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[1] Loss as phosphuretted hydrogen ; estimation of arsenic as phosphorus ; and errors due to large bulk of solutions employed. [2] 1866, **4,** 519.

large quantity of iron, as in many kinds of pig-iron, the whole dissolves in hydrochloric or dilute sulphuric acid, the phosphorus passing into solution as phosphoric acid." This statement is the very reverse of that made by M. Tantin, and to ascertain its accuracy I made the following experiment.

I had just finished an analysis of bar-iron which, by the ordinary method I used,[1] had given 0.124 per cent. phosphorus. I took 10 grams of this and dissolved it in hydrochloric acid, finally boiling the solution; neutralised with ammonia, and after adding a few cc. of permanganate to oxidise a little iron, precipitated basic acetates, boiling the filtrate twice for further precipitates; the combined precipitates were dissolved in hydrochloric acid, oxidised with nitric acid, precipitated with ammonia, and the precipitate redissolved in nitric acid, and the phosphorus precipitated with ammonium-molybdate, finally weighing the yellow precipitate. The result I obtained by this method was 0.122 per cent., which is a very satisfactory confirmation of the statement the experiment was meant to verify. The time taken in this determination was about from 5 to 6.30 P. M. one evening, by which time I had the yellow precipitate formed,[2] and the time necessary to filter and weigh the precipitate the next day, perhaps an hour more.

This result being so satisfactory, I treated some filings of a high-phosphorus pig (in which by my ordinary method I had found 0.826 per cent.) in the same manner, but found that I had only succeeded in obtaining 0.580 per cent., or about five-sevenths of the total amount present. I also prepared a button of very high-phosphorus iron, and on treating in the same way found that I only obtained about three-quarters of the amount present. This made me think that probably the loss was due either to the escape of phosphuretted hydrogen or to the formation of some other compound than phosphoric acid. I therefore arranged a simple apparatus, the same, in fact, which I use for the determination of sulphur in iron, which is filled with an atmosphere of hydrogen

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[1] Ten grams dissolved in 120 cc. nitric acid sp. gr. 1.20, evaporated to dryness and heated in air-bath to 120° to 130° C. several hours, redissolved in hydrochloric acid, reduced with ammonium bisulphite: precipitate the phosphoric acid by a basic acetate separation, boil the filtrate twice for further precipitates, making three in all, dissolve the combined precipitates in hydrochloric acid, filter out silica, oxidise solution with nitric acid, precipitate with ammonia, redissolve the precipitate in nitric acid, and ammonic molybdate. This last precipitate is redissolved in ammonia and reprecipitated by nitric acid, is then filtered on a Gooch crucible, dried and weighed, and afrerwards checked by precipitation as ammonic-magnesic phosphate.

[2] I did not seek to remove silica by evaporation to dryness. Per cent. Si = 0.151.

throughout the operation, and consists of a flask A to hold the acid, a flask B for the iron, and flasks C and D, of which C is generally left empty to catch condensed steam, and the two flasks D contain the absorbent liquid.
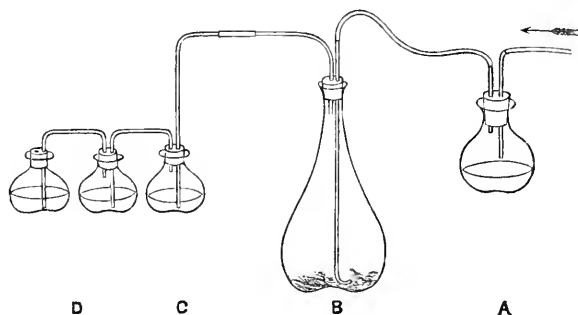
The absorbent liquid in D was a solution of potassium-permanganate acidified with nitric acid. The iron having been placed in B, and the necessary amount of dilute hydrochloric acid to dissolve it in A, the whole apparatus was filled with hydrogen, a current of which was kept passing through the whole time. When the air was all expelled the flask A was inverted above the level of B, so that its contents flowed into B, and the solution of the iron commenced. The solution was heated to boiling for some minutes, and when all had dissolved, with the exception of the insoluble portion, the apparatus was disconnected, the insoluble residue filtered from the solution, the solution divided into equal parts, one of which was oxidised with nitric acid and treated as in an ordinary determination of phosphorus, while the other was immediately precipitated by basic acetate, as in the first experiment described.[1] The amounts of phosphorus found in the prepared iron phosphide were distributed as below.

In residue, ... 3.79 per cent.

In solution { oxidised with nitric acid, 2.66
{ basic acetate direct,   2.16 per cent.

In gas, ... 0.05
                                   ————
                                  6.50

[1] Care being taken to remove silica wherever present.

. Showing a loss of 0.50 per cent. of phosphorus in the solution in some other form than phosphoric acid. It is very possible that nitric acid fails to oxidise to phosphoric acid all the phosphorus compounds formed in the solution. Referred to the total amount of phosphorus found (6.50 per cent.), the distribution per cent. is as follows:

In residue, ...	58.31
Recovered from basic acetate precipitation, . .	33.23
Lost, ...	7.69
In gas, ...	0.77
	100.00

I repeated the above process on a sample of pig-iron said to contain 0.885 per cent. phosphorus, and in which, by my usual method, I found 0.880 per cent. weighing as magnesia pyrophosphate, or, calculating from the weight of the yellow precipitate, 0.878 per cent. This was also conducted in a hydrogen atmosphere. The gas was caught in permanganate acidified with sulphuric acid in the first flask and with nitric acid in the second. Nearly all the phosphorus in the gas was retained in the first flask, a very small amount only passing over to the second. The results obtained were,

Phosphorus in residue, ...	0.345	per cent.
In solution { basic acetate precipitate, .	0.451	
{ lost, ...	0.065	
In gas, ...	0.019	
	0.880	

The distribution of the phosphorus is,

In residue, ...	39.11	per cent.
In solution { basic acetate precipitate, .	51.13	
{ loss, ...	7.60	
In gas, ...	2.16	
	100.00	

I then took a sample of high-phosphorus pig in which I had found in the usual way, 1.45 per cent. (weighed as yellow precipitate), or 1.48 per cent. (weighed as magnesia pyrophosphate), and dis-

solved 1 gram in 10 cc. hydrochloric acid and 30 cc. water, finally heating the solution to boiling. This time, instead of a stream of hydrogen being passed through the apparatus, a stream of oxygen was employed. The escaping gas was passed through permanganate and nitric acid. All the phosphorus caught was found in the first flask.

The residue, as in all these experiments, was heated with nitric acid and potassium chlorate; the solution was partially oxidised with 10 cc. permanganate (1 cc. = .01 Fe), and precipitated as basic acetate as usual; the silica separated from both portions, and the phosphorus determined. The total amount of phosphorus found was 1.42 per cent. weighed as magnesia pyrophosphate, or 1.37 per cent. weighed as the yellow precipitate, showing a loss of 0.06 per cent. The distribution of the phosphorus was,

In residue, ...		37.47 per cent.
In solution {	basic acetate precipitate, .	55.20
{	loss, ...	4.05
In gas, ...		3.28
		100.00

I next took 2 grams of the .880–.885 per cent. pig, and dissolved it, as in the last case, in a stream of oxygen, but instead of following up each portion separately, mixed them all together (the gas was caught in sulphuric acid permanganate), and collected the residue with the first basic acetate precipitate, treated with nitric acid and potassium chlorate, and proceeded as before. The phosphorus found was only 0.771 per cent., or of the total amount present, 87.41 per cent. was found and 12.59 per cent. lost.

I repeated the last experiment, using, however, dilute sulphuric acid in place of hydrochloric as the solvent, a stream of oxygen passing continually through, and the solution being kept boiling for fifteen minutes after all visible action had ceased. The total phosphorus found was 0.767 per cent., distributed as follows:

In residue, ...		14.17
In solution {	basic acetate precipitate, ...	70.86
{	loss, ...	13.16
In gas, ...		1.81
		100.00

These last two experiments showed that oxygen was not sufficient to convert the phosphorus in the forms lost into phosphoric acid; so the problem resolved itself into finding a method of converting the lower oxygen compounds of phosphorus into phosphoric acid, without simultaneously oxidising ferrous to ferric iron. The solution of this problem was obtained in the next trial. The process is the same as before described, using hydrochloric acid as the solvent, and a current of oxygen;[1] and after raising the solution to boiling, introducing an excess of a strong solution of sulphurous acid previously placed in the flask A, and continuing the boiling for some minutes. The result of the reaction is visible in the precipitation of sulphur in the solution, and the insoluble residue is much altered in appearance, being much more disintegrated. The results obtained in this experiment were: total phosphorus present, 0.882 per cent., weighed as magnesia pyrophosphate (care being taken to ensure its purity by resolution and reprecipitation of the magnesia precipitate), distributed

In residue, ... 13.49 per cent.
In solution, ... 80.84
In gas, ... 5.67
                                    ————
                                    100.00
Loss, ... 0.00

In confirmation of this result I made another determination in the same manner, starting at noon; by the following morning I found 0.865 per cent. of phosphorus, and had lost a small amount in the course of the rather hurried analysis.

The results obtained are given in tabular form on the next page.

I also made some confirmatory experiments on the sample used in experiment No. 5, weighing the yellow precipitate first obtained, instead of purifying it by reprecipitation. The precipitates carried traces of iron, which in experiments 11 and 12 entered into the magnesia precipitates. This explains discrepancies observable between the results calculated from the weights of the yellow precipitate and from those of the magnesic pyrophosphate.

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[1] The use of oxygen in place of hydrogen is recommended because it has no appreciable oxidising effect on the iron solution, while it prevents the reduction of the permanganate, which rapidly takes place with hydrogen.

Number.	Sample.	Per cent. P.	Method employed.	Per cent. P. found.			Total per cent. found.	Loss.	Per cent. distribution.			
				Residue.	Solution.	Gas.			Residue.	Solution.	Gas.	Loss.
1	Bar-iron.	0.124	Sol. in HCl and direct basic acetate precipitation.	0.122		...	0.122	0.002	...	98.4	...	1.6
2	Pig,	0.826	Sol. in HCl and direct basic acetate precipitation.	0.580		...	0.580	2.46	...	...	...	...
3	Iron phosphide,	6.50?	Sol. in HCl in H atmosphere. Gas absorbed in $K_2Mn_2O_8$ and HnO_3.	3.79	2.16	0.05	6.00	0.50	58.31	33.23	0.77	7.69
4	Pig,	0.880	Sol. in HCl in H atmosphere. Gas in $K_2Mn_2O_8$ +H_2SO_4.	0.345	0.451	0.019	0.815	0.065	39.11	51.13	2.16	7.60
5	Pig,	1.48	Sol. in HCl in O atmosphere. Gas in $K_2Mn_2O_8$ +HNO_3.	...	...	...	1.42	0.06	37.47	55.20	3.28	4.05
6	Pig,	0.880	Sol. in HCl in O atmosphere. Mixed all portions. Gas in $K_2Mn_2O_8$ +H_2SO_4.	...	...	...	0.771	0.109	...	87.41	...	12.59
7	Pig,	0.880	H_2SO_4 in O atmosphere and solution boiled 15 minutes.	...	...	...	0.767	0.111 *gain.*	14.17	70.86	1.81	13.16
8	Pig,	0.880	HCl in O atmosphere, boiled with excess SO_2.	...	...	...	0.882	0.002	13.49	80.84	5.67	0.00
9	Pig,	0.880	HCl in O atmosphere, boiled with excess SO_2, but all portions mixed.	...	...	...	0.865	0.015	Slight loss in course of analysis.			

Percentage P.	Old Method.	New Method.		
	No. 5.	No. 10.	No. 11.	No. 12.
Weighed as yellow precipitate, ...	1.447	1.49	1.451	1.463
No. of precipitations, . .	2	1	1	1
Weighed as $Mg_2P_2O_7$, .	1.480	1.456	1.516	1.539
No. of precipitations, . .	1	2	2	1

From inspection of this table it is seen that there is a far closer agreement between the results calculated from the weights of the yellow precipitate than in those calculated from the magnesic pyrophosphate ; and I am of the opinion that the true percentage of this sample is very near 1.454, the average of the four lowest results obtained.

In experiment 10 the phosphorus found was distributed—

In residue, ... 23.10
In solution, ... 73.00
In gas, ... 3.90
                                                        ————
                                                        100.00

In experiments 11 and 12 all portions were mixed together.

The following is a brief outline of the steps to be followed :

1. Solution in hydrochloric acid in a stream of oxygen or air, absorbing the escaping gases in permanganate acidified with sulphuric acid.

2. Heating the solution to boiling, stopping the passage of the oxygen current, and carefully adding an excess of sulphurous acid solution, and continuing the boiling till the precipitated MnO_2 in the absorption-flasks is redissolved. This boiling should last several minutes to ensure the completion of the reaction.

3. Disconnecting the junctions between the absorption-flasks and solution-flask, and between the solution-flask and the acid-flask, and allowing to cool.

4. Mixing solutions, filtering out residue, which is placed (with filter paper) in a porcelain casserole, oxidising with nitric acid and potassium chlorate, and evaporating to dryness.[1]

5. Boiling the solution till the excess of sulphurous acid is expelled, adding a few cc. of permanganate to peroxidise a little of the iron, and precipitating basic acetates. Boiling the filtrate for other precipitates, to ensure getting all the phosphoric acid present.

6. Dissolving these precipitates in hydrochloric acid, and adding to the solution of the residue in which, by this time, the paper will have been thoroughly destroyed.

7. Evaporating to dryness for silica, and proceeding as usual with the molybdate precipitation.

The saving of time by this process is the greater, as the percentage to be determined is less. In a steel of low percentage, where it is necessary to use 10 grams for the determination, necessitating the use of 120 cc. of nitric acid for solution, by the old method, the time taken for the evaporation of this amount of liquid, for the subsequent thorough drying of the residue, and for the resolution and reduction of the iron to the ferrous state, is evidently much greater, and the operations followed are much more tedious than by this method, where the phosphorus is concentrated at the start in but a few milligrams of iron in very little bulk of solution, enabling the subsequent evaporation to dryness, and thorough drying of the residue to be performed in a very short period.

In M. Tantin's experiments he used cast-iron only. Mine have been conducted on pig and wrought-iron. It is possible that the difference in our results may be partially accounted for by different modes of occurrence of phosphorus similar to the different forms of carbon, but of this I cannot speak from experience, and merely offer it as a suggestion.

The small amount of phosphuretted hydrogen which is found seems to be the product of a secondary reaction between phosphorous acid and the nascent hydrogen evolved. Whether hypophosphorous or hypophosphoric acids are present, or, indeed,

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[1] I prefer to filter out the residue instead of filtering it out with the first basic acetate precipitate, because it is difficult to work accurately on a muddy liquid, and because there is a probability of loss of phosphorus by the continued action of the hot acid solution on the residue, after the sulphurous acid has been expelled. By proceeding as directed, this chance of loss is removed. Perhaps some of the loss in the ninth experiment may be due to this cause, as the residue in that experiment was not separately treated.

whether phosphorous acid is present, I am at present unable to say, but the results obtained point to the presence in the solution, along with phosphoric acid, of one or more of these as the cause of loss. The use of sulphurous acid, however, oxidises these to phosphoric acid without affecting the iron, so that by this process a determination can be made in a day which formerly required several days.

In calculating the percentage of phosphorus from the weight of the yellow precipitate, I have used in all cases the figure of 1.63 per cent. phosphorus in the precipitate, and have thought it worth while to give the results I have obtained in two determinations I have recently finished. I prepared the yellow precipitate from phosphoric acid, precipitated in the usual manner with excess of molybdic acid. One of these precipitates (A) was purified from possible excess of molybdic acid by solution and reprecipitation ; the other (B) was analysed without going through this process. The magnesia precipitate obtained from A was also purified by solution and reprecipitation, while that from B was ignited and weighed direct. The results are given below.

	A.	B.
Weight of yellow precipitate dried at 95°–100° C.	1.2802	1.1428
Weight of $Mg_2P_2O_7$,	.0735	.0664
Weight of P calculated from $Mg_2P_2O_7$,	.02053	.01854
Percentage of P in yellow precipitate,	1.603	1.623
Weight of P calculated from yellow precipitate, assuming factor 1.63 per cent.	.02087	.01863

ON THE DETERMINATION OF DIASTATIC ACTION.

By J. R. Duggan.

The various processes in which starch is converted into sugar by the action of disastase make it necessary to have some accurate method by which the converting power of any substance containing this ferment may be determined. Many of the results that have hitherto been published have undoubtedly been obtained

in such a manner that they are not even approximately correct. This has probably been due, not so much to the method employed, as to a disregard of the influence of very minute quantities of various substances, and consequently to a lack of care in the selection of pure reagents.

As diastase cannot be entirely separated from other substances, it is impossible to determine the actual amount present, but the comparative amount may be found by ascertaining the quantity of starch converted into sugar under known conditions.

This power of conversion is known as the " diastatic value " of any substance. The principal conditions affecting the extent of conversion are time, temperature, and the presence of various foreign substances, such as acids, alkalis, etc. The influence exerted by these has already been investigated to some extent by Kjeldahl[1] and others. It has also been shown by Bert[2] that pressure does not influence this reaction.

The method usually adopted for measuring the extent of conversion has been to determine the amount of sugar formed ; but some have preferred—probably because it involves less labor—to determine the time required for the conversion into dextrin and sugar of a given weight of starch—using iodine as an indicator. This method is inaccurate, for the following reasons. The rate of conversion, as will be seen later, is not quite proportionate to the time of action ; but even if this were true, it is not practicable by means of iodine to fix the time of the disappearance of the starch. This is due to the fact that the dextrin present gives a color with iodine, and there is no time during the reaction at which the blue color suddenly fails to appear when iodine is added, but the blue gradually shades into a purple, and this into a rose color, the intensity of these depending upon the amount of iodine added, as well as on the extent of conversion.

Except when otherwise stated, the following details have been observed in making the determinations described in this paper. The starch paste was made by adding 6 grams of air-dried arrow-root ($=$ 5.420 grams dried at 110°) to 200 cc. of distilled water, and heating the mixture in a water-bath until the starch was thoroughly gelatinised. The flask containing this was then placed in a large water-bath, which was kept at a constant temperature ;

[1] Ding. Polytech. J. **235**, 379 and 452 ; also Centralblatt **11**, 73.

[2] Compt. Rend. **80**, 1579.

and when the starch paste had acquired the temperature of the surrounding water, the requisite quantity of a solution of malt extract was added, and the solutions well mixed by shaking. When it became necessary to stop the reaction, 2 cc. of a 10 per cent. solution of caustic soda were added. The whole was then diluted to a given volume, and the sugar determined as maltose, volumetrically, by Fehling's solution. The errors of this method were found to be too slight to affect the value of results, while the somewhat more accurate method of weighing the precipitated copper oxide was not practicable, in view of the large number of determinations to be made. Arrow-root was used on account of its freedom from alkali, which is usually present in starches made from corn or potatoes. This is due to the use of caustic soda in their extraction and incomplete washing afterwards. In fact it is difficult even by a long washing to remove all the alkali present, and it is probable that a small amount is absorbed and held in combination by the granules, as has been shown to be the case with cellulose.[1] The following table shows the amount of sugar formed from several samples of starch :

No.	Maltose.	No.	Maltose.
1	0.098 gram.	4	0.475 gram.
2	0.328	5	1.423
3	0.135	6	2.010

5 cc. malt solution.   Time, 30 minutes.   Temperature, 55°.

The first four of these were ordinary laundry starches of different manufacture, the fifth was a corn starch for culinary purposes, and the sixth was arrow-root. Four other samples of arrow-root were examined, and they all gave results agreeing very closely with this one, so it seems that this starch is sufficiently uniform for general use in diastatic determinations.

Distilled water must also be used in making the starch paste and the malt solution. The substitution of hydrant water from the city water supply was found to diminish the conversion by about 40 per cent., this not being quite constant. A sample of rain water was also found to retard the action of the diastase to the extent of 11 per cent. From these facts it will be seen how great care must be exercised to obtain pure reagents. The use of water redistilled

[1] Mills. J. Chem. Soc. **43**, 142.

from potassium permanganate was found to be unnecessary, as it made no appreciable difference in results.

The malt solution used was a 5 per cent. solution of a commercial extract. A minute quantity of free acetic and lactic acids present (amounting usually to about 0.01 gram NaOH to 100 cc.) was carefully neutralised with caustic soda. In making analyses for commercial purposes this precaution is scarcely necessary, for when the usual quantity of malt solution is added to the starch paste, the dilution is so great that the very minute quantity of acid present could cause only a very slight error. The solution under examination should, however, always be examined, for there might be present a much larger amount of free acid, especially if fermentation has taken place. In such a case it should, of course, be neutralised.

The Influence of Acids and Alkalis on Diastatic Action.

It has already been seen from the experiments on various starches that diastase is very much retarded in its action by the presence of quite small amounts of alkali. The diminished conversion when ordinary water is used seems to be due to slight alkalinity also. The following table shows the effect of very minute quantities of caustic soda :

Parts of NaOH per 1,000,000 of starch paste.	Maltose.
0	1.992 grams.
10	1.578
15	0.921
20	0.520

Malt solution, 5 cc. Time, 30 minutes. Temperature, 55°.

There is very little or no conversion when somewhat greater quantities of alkali are used. The proportion of caustic soda to the starch in these experiments was respectively 0.033, 0.050 and 0.066 of one per cent. The effect of carbonates and other alkaline salts I have not yet investigated.

My experiments on the influence of acids have led me to doubt the general statement that diastase acts best in a slightly acid medium ; or, if this is true, the amount of acid required for this is certainly very much more minute than is usually stated, as is shown by the following table :

Parts of H_2SO_4 per 1,000,000 of starch paste.	Maltose.
0	2.003 grams.
5	2.035
10	1.913
20	1.053

Malt solution, 2 cc.   Time, 1 hour.   Temperature, 55°.

There is here an increase in sugar production of only 1.5 per cent. when 0.0005 of one per cent. of sulphuric acid is used, which at first sight seems to be due to the favorable action of the acid on the diastase, but I am inclined to think that this would not take place with perfectly pure starch.   The starch used in these experiments, while perfectly neutral, made the reaction of the litmus less sharp, owing, no doubt, to certain salts contained in the granules, and which could not be entirely washed out with water alone.   If an acid was added to the wash water it only complicated matters, by remaining itself in combination with the starch.   As the amount of acid which increased the conversion was equal to only $\frac{1}{6000}$ of the starch used, it is very possible that this does not remain free, but enters into combination with certain salts naturally present in the starch.   This, together with the fact that 0.001 of one per cent. of acid considerably retards the conversion, makes it appear probable that diastase acts as rapidly on pure starch as in an acid solution.   I hope, however, to decide this point more definitely, using soluble starch that has been purified by repeated precipitation.   Diastase will also be prepared as pure as possible, and used instead of malt extract, which, of course, contains phosphates and other salts that may affect the reaction.   A closer study of this point will perhaps be of use in fixing the conditions necessary to obtain a proper and uniform action of diastase in the mash tub. The statement of Jungk[1] that diastase is much more active in a solution containing 0.033 of one per cent. of hydrochloric acid is certainly incorrect, and is probably due to the use of alkaline starch.   If this were true, it is not probable that a slight increase of this amount (0.05 of one per cent.) would, as he states, entirely prevent conversion.

Influence of Time on Diastatic Action.

In the first series of experiments on this point a specimen of ordinary starch containing alkali was used, and the rate of sugar

[1] Phar. J. Trans. (3) **14**, 104.

production was found to decrease rapidly as the time advanced ; but when neutral starch was used this was not the case. The only explanation of this fact seems to be that the effect of the alkali increases with the time of exposure. When the solution is neutral, the amount of starch converted is almost directly proportional to the time of action, as is shown by the following table :

Time.	Maltose.	Conversion per min.
5 minutes.	0.214 gram.	0.0428 gram.
10	0.416	0.0416
20	0.806	0.0403
40	1.593	0.0398
60	2.033	0.0339

Malt solution, 2 cc. Temperature, 55°.

The decrease in the rate of conversion shown in the last experiment of this series is not due to a lessening of the activity of the diastase, but to the fact that over one-third of the starch had been converted into maltose. As is shown later, the reaction is always retarded under these circumstances. A series of experiments extending over a longer time gave the following results :

Time.	Maltose.	Conversion per min.
1 hour.	2.284 grams.	0.038 gram.
2 hours.	4.301	0.035
2 hours 30 minutes.	5.257	0.035

Malt solution, 2 cc. Temperature, 55°. 500 cc. of 3.5 per cent. starch paste.

The fact that the extent of conversion is not quite proportional to the time of action is probably due, merely, to the gradual dilution of the starch paste, owing to the change which is taking place ; and if the starch was replaced as fast as it was converted, there is every reason to suppose that the diastase would continue its action indefinitely. It is not therefore, as Baswitz[1] has claimed, used up in the reaction ; and it is probable that the same is true of the other soluble ferments. These results also seem to show that the starch molecule breaks up directly into dextrin and maltose, and not into dextrin first and this into maltose; for if this was the case, in the first part of the time during which the dextrin was forming there should be formed little or no maltose, while later the production of maltose should become more rapid.

[1] Berichte **11**, 1443.

The Influence of the Amount of Diastase on the Rate of Conversion.

The statement of Baswitz[1] that with a given amount of starch the conversion was not proportional to the amount of diastase, has been shown by Kjeldahl[2] to be incorrect, provided the quantity of maltose formed is not greater than 45 per cent. of the starch used. The results obtained by Kjeldahl do not, however, show very close agreement, since he found that on using three times the quantity of malt solution, the proportionate extent of conversion was diminished by from 10 to 17 per cent.

The action seems to be slightly diminished when the amount of diastase is increased; but this, within ordinary limits, amounts to a very small percentage. The starch converted into maltose should not exceed 35 per cent. of the whole amount, and it is better that it should not be less than 5 per cent., as in this case the large quantity of starch left in solution interferes with the precipitation of the copper oxide. The extent of conversion produced by varying amounts of malt solution is shown in the following series of experiments :

Malt Solution.	Maltose.	Conversion per cc.
1 cc.	0.475 gram.	0.475 gram.
2	0.937	0.469
3	1.381	0.460
5	2.269	0.454
7	2.790	0.399
10	3.196	0.320

Time, 30 minutes.   Temperature, 55°.

The effect of a too small excess of starch is shown in the last two of these experiments.

The temperature of 55° C. is best suited for diastatic determinations, for not only does the greatest action take place at about this degree, but any accidental variation of two or three degrees either above or below 55° will make no appreciable difference in the amount of sugar formed. The experiments given in this paper have all been performed at this temperature, but a sufficient number have been made at other temperatures to show that the facts established are not confined to any temperature at which there is action, provided it is not so high as to injure the diastase.

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[1] Berichte **12**, 1827.   [2] Ding. Polytech. J. **235**, 379.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

By Wolcott Gibbs, M. D.

Rumford Professor in Harvard University.

(Continued from p. 238.)

ARSENOSO-TUNGSTATES.

The alkaline salts belonging to this series are easily prepared by boiling arsenous oxide with strong solutions of acid tungstates, as, for example, with 12 : 5 or 10 : 4 sodic salt.   The arsenous oxide should be in excess to secure complete saturation.   The filtered solution on standing usually deposits crystals of arsenous oxide in greater or less quantity.   The salts of this series are either colorless or pale yellow.   They are not very easily oxidised in acid solutions, but in presence of an excess of alkali they absorb oxygen from the air and are converted into arsenio-tungstates. Bromine and chlorine readily oxidise such solutions.   The arsenoso-tungstates are, as a rule, more soluble than arsenio-tungstates.   They are very stable and well defined, and may as a class be embraced under the general formula

$$m\mathrm{WO_3}.n\mathrm{As_2O_3}.p\mathrm{R_2O},$$
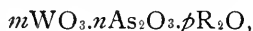
in which n is usually greater than unity.

Analytical Methods.—Hydric sulphide precipitates arsenous sulphide from these salts, and usually without sensible reduction of the tungstic teroxide.   It is best to precipitate from a hot solution, and to pass the current of the gas for a long time to insure complete decomposition.   The arsenous sulphide may then be collected and weighed upon a Gooch asbestos filter.   The tungstic oxide may be determined in the filtrate by mercurous nitrate in the usual manner.   The simplest and most satisfactory method of determining the arsenic is by titration with iodine in a solution containing an excess of sodic or potassic bicarbonate. Finally, it is possible to determine the arsenic by oxidising the solution with bromine after adding an excess of an alkaline carbonate, and then precipitating the arsenic in the form of ammonio-magnesic arsenate.   The precipitate must be redissolved in dilute chlorhydric acid and precipitated a second time.

The alkaline arsenoso-tungstates are, as a rule, easily soluble; the crystalline salts are often soft and gummy, though well defined.

They appear in some cases to be decomposed more or less completely by solution and evaporation, with separation of arsenous oxide and formation of new salts of different series. In certain cases the addition of a salt of one of the heavy metals determines the precipitation of crystals of arsenous oxide in quantity. It is well known that alkaline hydrates also dissolve arsenous oxide in a proportion more than sufficient to form definite salts, and that the solutions deposit crystals of arsenous oxide on standing.

9 : 1 *Ammonic Arsenoso-tungstate.*—A boiling strong solution of 12 : 5 sodic tungstate dissolves arsenous oxide very readily, and in large quantity. The solution on evaporation gives a colorless or very pale yellow thick gummy mass, which on re-solution leaves octahedral crystals of arsenous oxide. The solution of the sodic salt gives with ammonic chloride, after standing some time, beautiful pale yellow almost colorless prisms. These may be redissolved and recrystallised without decomposition. Of this salt,

1.2699 gram lost on ignition 0.2750 gram $= 21.65$ per cent. H_2O, As_2O_3, and NH_3.

1.3508 gram gave by titration with iodine 0.1034 gram As_2O_3 $= 7.65$ per cent.

1.9457 gram gave 0.2713 gram $NH_4Cl = 6.78$ per cent. $(NH_4)_2O$.

0.9776 gram gave 0.7732 gram $WO_3 = 79.09$ per cent. by $Hg_2(NO_3)_2$ and ignition.

The analyses lead to the formula

$$18WO_3.2As_2O_3.7(NH_4)_2O + 18Aq,$$
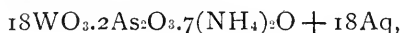
which requires :

		Calculated.	Found.
$18WO_3$	4176	79.39	79.09
$2As_2O_3$	396	7.53	7.65
$7(NH_4)_2O$	364	6.92	6.78
$18H_2O$	324	6.16	6.48
	5260	100.00	

The salt may of course be regarded as a double salt, but in this class of salts, as in the arsenio-tungstates and phospho-tungstates, I am disposed to think that in all cases we have an even number of molecules of tungstic oxide united with at least *two* molecules of arsenous oxide. Further investigations are of course required to settle this question. Meantime, from the analogy of the baric salt, we may write the formula provisionally as

$$9WO_3.As_2O_3.4(NH_4)_2O + 9WO_3.As_2O_3.3(NH_4)_2O + 18Aq.$$

9 : 1 *Baric Arsenoso-tungstate.*—A solution of sodic arsenoso-tungstate obtained as above gives a white crystalline precipitate with baric chloride which is nearly insoluble in water, and which was therefore only washed upon the filter and dried on woollen paper for analysis. In this salt,

1.1037 gram ignited with WO_4Na_2 lost 0.1290 gram $=$ 11.69 per cent. H_2O.

1.9764 gram titrated with iodine gave 6.15 per cent., 6.38 per cent., 6.18 per cent. As_2O_3, mean 6.23 per cent.

1.5652 gram gave 0.4358 gram $SO_4Ba =$ 18.28 per cent. BaO.

In determining the arsenous oxide the salt was first dissolved in very dilute chlorhydric acid, an excess of sodic bicarbonate being added before titration. The analyses correspond with the formula

$$9WO_3.As_2O_3.4BaO + 21Aq,$$
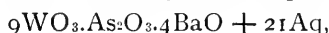
which requires:

		Calculated.	Found.
$9WO_3$	2088	63.74	63.80
As_2O_3	198	6.04	6.23
$4BaO$	612	18.68	18.28
$21H_2O$	378	11.54	11.69
	3276	100.00	

The formula may be

$$18WO_3.2As_2O_3.8BaO + 42Aq.$$
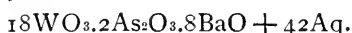
I have stated above that arsenoso-tungstates pass readily into arsenio-tungstates by oxidation and assumption of two additional atoms of oxygen. It seemed, therefore, natural to suppose that other simple or complex molecules might also be added to the molecule of arsenous oxide entering into the complex acid. I shall hereafter give the results of a detailed examination of this subject.

16 : 8 *Sodic Arsenoso-tungstates.*—Arsenous oxide dissolves readily in 10 : 4 sodic tungstate on boiling. When an excess of arsenic is present, the filtrate, after evaporation to the consistency of a syrup, deposits on spontaneous evaporation large colorless prismatic crystals. These dissolve readily in water without decomposition, and may be recrystallised until perfectly pure. After four recrystallisations,

0.9451 gram gave with CO_3NaH and iodine 0.2178 gram As_2O_3 $=$ 23.05 per cent.

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0.6128 gram gave with CO_3NaH and iodine 0.1416 gram As_2O_3 $= 23.10$ per cent.

1.1327 gram gave 0.3237 gram $As_2S_3 = 23.01$ per cent. As_2O_3.

0.9225 gram gave 0.5005 gram $WO_3 = 54.26$ per cent.

1.0614 gram gave 0.5781 gram $WO_3 = 54.46$ per cent.

0.8517 gram gave 0.1238 gram $H_2O = 14.54$ per cent.

The analyses agree well with the formula

$$16WO_3.8As_2O_3.9Na_2O + 55Aq,$$
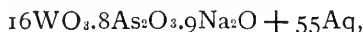
which requires:

		Calculated.	Found.		
$16WO_3$	3712	54.23		54.28	54.46
$8As_2O_3$	1584	23.14	23.05	23.10	23.01
$9Na_2O$	558	8.16		8.04 (diff.)	
$55H_2O$	990	14.47		14.54	
	6844	100.00			

The salt gives off vapors of arsenous oxide even on gentle heating, and the determination of the water cannot be made by the use of sodic tungstate. After many trials, it was found best to mix the salt in a porcelain boat with plumbic oxide and carefully heat in a combustion tube, collecting the water in asbestos drenched with sulphuric acid. This process, suggested by my assistant, Mr. Herman Schmidt, gave good results in this case. A solution of the salt gives white flocky crystalline precipitates with baric, strontic and calcic chlorides. Mercurous nitrate gives a pale yellow precipitate, which becomes darker on heating, and finally takes a dirty greenish-white color. Argentic nitrate gives a milk-white precipitate, which remains suspended for a long time. Manganous sulphate gives no precipitate, but the solution becomes yellow, and after standing some time, yields beautiful bright yellow tabular crystals. Ammonic and potassic arsenates and orthophosphates give white crystalline precipitates, which appear to be respectively arsenoso-arsenio-tungstates and arsenoso-phospho-tungstates. The mother liquor of the 16 : 8 salt gives on evaporation a few crystals in a thick colorless syrup, which, after a few days, forms a pale yellowish hard gummy mass. This may prove to contain a second arsenoso-tungstate. The best method of preparing the beautiful 16 : 8 salt in quantity will probably be to mix 12 : 5 or 10 : 4 sodic tungstate and arsenous oxide in the precise ratio indicated by the formula of the salt,

and, after adding water, to boil until the arsenous oxide is dis-
solved.

ARSENOSO-MOLYBDATES.

Arsenoso-molybdates are formed under the same conditions as
arsenoso-tungstates, by boiling solutions of acid molybdates with an
excess of arsenous oxide. In this case also there is always a sort
of supersaturation, and arsenous oxide separates from the solution
on cooling. The general statements made concerning the arsenoso-
tungstates apply to these salts also. The general formula is

$$m\mathrm{MoO_3}.n\mathrm{As_2O_3}.p\mathrm{R_2O},$$

in which n is usually greater than unity. The salts are often
beautifully crystalline.

Analytical Methods.—Arsenous oxide may be determined in
these salts by oxidising the solutions in presence of an excess of
an alkaline carbonate by means of bromine, and precipitating as
ammonio-magnesic arsenate. The precipitation must be repeated
a second time, but the final treatment with ammonic sulphide,
which I have recommended for the separation of phosphoric and
molybdic oxides, is of course inadmissible. By far the best
method of determining the arsenic in these salts is titration with
iodine after addition of an excess of an alkaline bicarbonate. It is
not possible to determine the oxides of molybdenum and arsenic
together by precipitation with mercurous nitrate, since no amount of
care suffices to prevent the volatilisation of arsenic in the subsequent
ignition. For the same reason, it is also very difficult to determine
the water of crystallisation by the ignition loss, as fumes of arsenous
oxide are given off at temperatures which are much below that at
which sodic tungstate fuses. The degree of facility with which
this takes place varies with the salt to be analysed. As regards the
determination of the water, I have found it best to heat gently in a
porcelain crucible, supported over a small iron cup heated from
below, but even in this case the results are never very satisfactory.
Arsenous oxide cannot be separated from molybdic oxide by
hydric sulphide, since molybdic sulphide is always precipitated at
the same time, even when phosphoric acid has been added in
excess. I have, however, found that fairly good determinations of
molybdic oxide may be made in many cases by dissolving, boiling
with a small excess of ammonia, adding a little ammonic chloride,
and finally precipitating with baric chloride. The baric molybdate

may then be ignited and weighed upon an asbestos filter. The results, if not very accurate, are at least sufficiently close to be of great service as verifications of formulas.

8 : 2 *Baric Arsenoso-molybdate.*—A boiling strong solution of 14 : 6 ammonic molybdate dissolves arsenous oxide in large quantity, and very readily. The solution has usually a yellowish-green color from slight reduction of the molybdic teroxide. After filtration and evaporation upon a water-bath, it deposits an abundance of octahedral crystals of arsenous oxide. The filtrate from these does not yield crystals on standing, but after evaporation upon the water-bath solidifies to a greenish gummy mass, readily soluble in water, often, however, leaving a residue of arsenous oxide. The solution of this gummy salt gives a white crystalline precipitate with baric chloride. The filtrate from this, after evaporation and standing, yields an abundance of beautiful very pale greenish crystals, which may be redissolved and recrystallised without decomposition.   In this salt,

1.1230 gram lost on heating 0.1126 gram $=$ 10.03 per cent.
1.0548 gram gave 0.3258 gram $SO_4Ba =$ 20.28 per cent. BaO.
0.3919 gram gave 0.0678 gram $As_2O_3 =$ 17.31 per cent.
0.5774 gram gave 0.0995 gram $As_2O_3 =$ 17.23 per cent.
0.9729 gram gave 1.0383 gram $MoO_4Ba =$ 51.74 per cent. MoO_3.
The analyses lead to the formula

$$8MoO_3.2As_2O_3.3BaO + 13Aq,$$
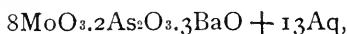
which requires :

		Calculated.	Found.
$8MoO_3$	1152	$\left.\begin{matrix}51.41 \\ 17.67\end{matrix}\right\}$ 69.08	$\left.\begin{matrix}51.74 \\ 17.31 \quad 17.23\end{matrix}\right\}$ 69.01
$2As_2O_3$	396		
$3BaO$	459	20.48	20.28
$13H_2O$	234	10.44	10.03
	2241	100.00	99.32

The arsenous oxide was determined in the first analysis by boiling with a solution of sodic dicarbonate, filtering, and titrating with iodine; in the second, by direct titration without previous filtration. The baryta was separated by fusion with sodic carbonate, and weighed as sulphate. The water was found by heating over a radiator until a constant weight was obtained, as it was impossible to ignite with sodic tungstate without volatilisation of arsenous oxide.

The salt requires a very large quantity of water for solution. The dry salt in fine powder boiled with argentic nitrate gives a beautiful yellow crystalline salt. Thallous nitrate yields, under the same circumstances, a very pale yellow, also crystalline salt. The mercurous salt is pale yellow, but not distinctly crystalline.

12 : 5 *Arsenoso-molybdate of Ammonium.*—When a solution of zincous sulphate is added to one of the gummy arsenoso-molybdate of ammonium, no precipitate is found at first, but after a time colorless crystals are formed which do not contain zinc, and which may be recrystallised without apparent decomposition. The salt dissolves in a large quantity of water to a colorless solution. It is only partially decomposed by boiling with mercurous nitrate. In this compound,

0.7105 gram gave 0.0326 gram $(NH_4)_2O = 4.58$ per cent.
0.9785 gram gave 0.0455 gram $(NH_4)_2O = 4.65$ per cent.
1.2612 gram gave 1.3720 gram $MoO_4Ba = 52.74$ per cent. MoO_3.
1.3081 gram gave 0.3856 gram $As_2O_3 = 29.48$ per cent.
0.6044 gram gave 0.1787 gram $As_2O_3 = 29.55$ per cent.

The analyses correspond fairly well with the formula

$$12MoO_3.5As_2O_3.3(NH_4)_2O + 24Aq,$$
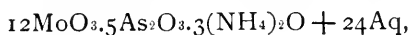
which requires:

		Calculated.		Found.		
$12MoO_3$	1728	52.28 } 82.21		52.74 } 82.24		
$5As_2O_3$	990	29.94		29.48	29.55	
$3(NH_4)_2O$	156	4.71		4.58	4.65	
$24H_2O$	432	13.07		13.15		
	3306	100.00				

The reactions of this salt were studied by acting with metallic solutions upon the finely pulverised substance, so as to avoid, if possible, the decomposing action of water. In this manner cold solutions of argentic and thallous nitrates give beautiful colorless granular crystals. Baric chloride gives a white colorless salt more flocky than the ammonium compound. Manganous sulphate does not react in the cold, but on boiling for some time, a beautiful pale canary-yellow crystalline salt is formed. Cupric sulphate does not act when cold, but on boiling a clear solution results.

6 : 3 *Arsenoso-molybdate of Manganese.*—A portion of the dry gummy mass of arsenoso-molybdate of ammonium, which had stood for some time in the laboratory, was redissolved and filtered

from a small quantity of arsenous oxide. The filtrate gave no pre-
cipitate with manganous sulphate, but, on boiling, the fine green
solution became much lighter in color, then turbid, and finally
deposited very beautiful bright orange-colored octahedral crystals
insoluble in water. Of this salt,

0.5961 gram gave 0.2052 gram $As_2O_3 = 34.41$ per cent.

0.7341 gram gave 0.1216 gram $P_2O_7Mn_2 = 8.28$ per cent. MnO.

0.6362 gram lost on heating over a radiator 0.0428 gram $= 6.73$
per cent.

The analyses correspond to the formula

$$6MoO_3.3As_2O_3.2MnO + 6Aq,$$
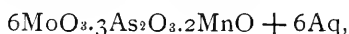
which requires:

		Calculated.	Found.
$6MoO_3$	864	50.59	50.58
$3As_2O_3$	594	34.78	34.41
$2MnO$	142	8.31	8.28
$6H_2O$	108	6.32	6.73
	1708	100.00	

The molybdic oxide was determined by difference only. By
mixing a solution of the gummy arsenoso-molybdate of ammonium
with solutions of zincous and cupric sulphates respectively, after
standing, beautiful octahedral crystals were deposited, which in the
case of the zinc salt were colorless, in that of copper, of a fine
green. The corresponding nickel salt was also in beautiful green
octahedral crystals. In the zinc salt,

0.2378 gram gave 34.52 per cent. As_2O_3 by titration with iodine.

0.3115 gram gave 34.47 per cent. As_2O_3 by titration with iodine.

0.2169 gram gave 34.56 per cent. As_2O_3 by titration with iodine.

The formula

$$6MoO_3.3As_2O_3.2ZnO + 6Aq$$
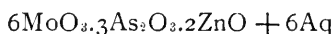
requires 34.38 per cent. In the copper salt,

0.2619 gram gave 34.67 per cent. As_2O_3 by titration with iodine.

0.2006 gram gave 34.89 per cent. As_2O_3 by titration with iodine.

The formula

$$6MoO_3.3As_2O_3.2CuO + 6Aq$$
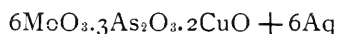
requires 34.41 per cent.

In the cases of both the zinc and copper salts a trace of free
arsenous oxide was probably mixed with the salt analysed. The

nickel salt doubtless corresponds to the other three. In the case of the manganese salt, fumes of arsenous oxide were given off at very low temperatures. The pale canary-yellow manganese salt obtained by precipitating the $12:5$ ammonic salts with manganous sulphate corresponded to the formula

$$6MoO_3.3As_2O_3.2MnO + 15Aq.$$
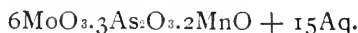
0.1727 gram gave 31.77, 31.62 and 31.73 per cent. As_2O_3 by titration with iodine.

1.1393 gram gave 0.0898 gram $Mn_3O_4 = 7.33$ per cent. MnO.

The formula given requires 31.77 per cent. As_2O_3 and 7.59 per cent. MnO. The salt gave off arsenous oxide very freely when heated with sodic tungstate.

PHOSPHOROSO-TUNGSTATES.

I have already described the class of phosphoroso-molybdates, and will now consider the parallel group of phosphoroso-tungstates. The alkaline salts of this series are readily formed by the action of phosphorous and chlorhydric acids upon metatungstates of the higher order. They are, as a rule, better defined than the corresponding phosphoroso-molybdates, and are in all probability very numerous. The compounds to be described will be sufficient to open the subject for further investigation. The analytical methods employed were the same as in the case of the corresponding molybdenum salts, except that after oxidation of phosphorous to phosphoric acid, tungsten and phosphorus were usually precipitated together by mercurous nitrate and mercuric oxide.

$22:4:6$ *Ammonic Phosphoroso-tungstate.*—When the solution of phosphorous and chlorhydric acids formed by the action of water upon phosphoric terchloride is poured upon crystalline $12:5$ ammonic tungstate, the salt packs at once into a dense mass. This is to be well rubbed up in a mortar with a large excess of the acid liquid, and allowed to stand for twenty-four hours. The greater part of the mass then presents large granular colorless crystals. A much smaller proportion of a white fine-grained salt is formed at the same time, and is easily separated by washing from the heavier crystals of the granular salt. This last may be washed with cold water on the filter pump, and dried on woollen paper. In mass the crystals present a faint but distinct tinge of yellow. The salt is but slightly soluble in cold water, but dissolves

in a rather large proportion of boiling water to a yellow liquid. The solution gives no precipitate with cupric sulphate, but the mixed liquid becomes somewhat darker on boiling. With argentic nitrate it gives a turbid solution, which becomes purplish on heating, and finally gives a dark dull-purple precipitate. With mercurous nitrate the solution gives a white light precipitate, which becomes deep yellow on heating, and regains its white color on cooling. In this salt,

1.6407 gram gave 0.1136 gram $P_2O_7Mg_2 = 5.12$ per cent. PO_3H_3.

1.7666 gram gave 0.1256 gram $P_2O_7Mg_2 = 5.26$ per cent. PO_3H_3.

1.5933 gram gave 0.0791 gram $(NH_4)_2O = 4.96$ per cent.

1.7340 gram lost with WO_4Na_2 0.2253 gram $= 12.99$ per cent.

The analysis is of course subject to the corrections indicated by the equation

$$2PO_3H_3 = P_2O_5 + OH_2 + 4H.$$
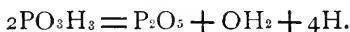
The results agree very well with the formula

$$22WO_3.4PO_3H_3.6Am_2O + 25Aq,$$

or

$$22WO_3.4[H.PO.2OH] 6(NH_4)_2O + 25Aq,$$
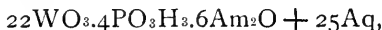
which requires :

		Calculated.	Found.	
$22WO_3$	5104	82.40	82.46	
$4PO_3H_3$	328	5.29	5.26	5.12
$6(NH_4)_2O$	312	5.04	4.96	
$25H_2O$	450	7.27	7.32	
	6194	100.00		

The phosphorous acid was oxidised by bromine after adding an excess of sodic carbonate. The salt is quietly decomposed by heating, giving a mixture of $WO_3.W_2O_5$ and P_2O_5.

32 : 16 : 5 *Potassic Phosphoroso-tungstate.*—This salt was formed, like the ammonium salt, by the action of a mixture of phosphorous and chlorhydric acids upon crystallised 10 : 4 potassic tungstate. In this case also, two salts appear to be formed—a heavier colorless crystalline salt in relatively large quantity, and a lighter fine-grained salt easily removed by careful washing. Of these only the first was examined. Of this salt,

1.4225 gram gave 1.2124 gram oxides $= 85.23$ per cent. $WO_3 + P_2O_5$.

1.3877 gram gave 0.2428 gram $P_2O_7Mg_2 = 11.19$ per cent. P_2O_5 = 12.96 per cent. PO_3H_3.

1.3949 gram lost 0.1406 gram = 10.08 per cent.

The analyses correspond to the formula

$$32WO_3.16PO_3H_3.5R_2O + 46Aq,$$

or

$$32WO_3.16[H.PO.2OH]5R_2O + 46Aq,$$
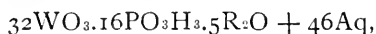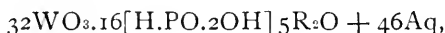
which requires:

		Calculated.	Found.
$32WO_3$	7424	73.97	74.04
$16PO_3H_3$	1312	13.07	12.96
$5R_2O$	472	4.70	4.69 (diff.)
$46H_2O$	828	8.26	8.31
	10036	100.00	

The salt is but slightly soluble even in boiling water. It has no yellow tint.

22:8:2 *Sodic Phosphoroso-tungstate.*—This salt was formed, like the last, by the action of a mixture of phosphorous and chlorhydric acids upon crystallised 10:4 sodic tungstate. The action is very energetic. The colorless crystals of the tungstate soon disappear, and are replaced by yellow granular crystals in large quantity. The yellow crystals were well washed upon the filter-pump with cold water, and dried on woollen paper. Of this salt,

1.7082 gram gave 1.4895 gram oxides = 87.19 per cent. WO_3 + P_2O_5.

1.3623 gram gave 0.1870 gram $P_2O_7Mg_2 = 8.78$ per cent. P_2O_5 = 10.15 per cent. PO_3H_3.

1.3532 gram lost with WO_4Na_2 0.1481 gram = 10.94 per cent.

The analyses correspond to the formula

$$22WO_3.8PO_3H_3.2Na_2O + 35Aq,$$
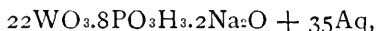
which requires:

		Calculated.	Found.
$22WO_3$	5104	78.36	78.40
$8PO_3H_3$	656	10.07	10.15
$2Na_2O$	124	1.90	1.87 (diff.)
$25H_2O$	630	9.67	9.58
	6514	100.00	

Gibbs.

The sodium salt is nearly insoluble in cold water, and but slightly soluble in boiling water. The undissolved portion takes a much brighter yellow color. As in the cases of the potassium and ammonium salts, a small quantity of a second salt, in very small crystals and of a white color, is formed at the same time.

PHOSPHOROSO-MOLYBDATES (*again*).

As the phosphoroso-molybdate of ammonium, which I have described in another part of this paper, appeared to contain a trace of phosphoric acid, I repeated the preparation with a perfectly pure solution of phosphorous acid obtained by the action of water upon phosphorous chloride. The liquid contained, of course, free chlorhydric acid, and was poured into a cold strong solution of $14:6$ ammonic molybdate. A sulphur-yellow precipitate was at once formed, consisting of very minute talcose scales. The salt was washed on the filter-pump very thoroughly with cold water, and dried on woollen paper. It is readily soluble in hot water to a yellow liquid. The solution on boiling reduces mercuric chloride to mercurous chloride. It gives an abundant white, flocky precipitate with argentic nitrate, which on long boiling becomes darker. Finally, silver is reduced. In this preparation,

0.7247 gram lost with WO_4Na_2 0.1150 gram $= 15.87$ per cent.

0.8323 gram gave 0.0386 gram $(NH_4)_2O = 4.64$ per cent.

0.7426 gram gave 0.0776 gram $P_2O_7Mg_2 = 6.68$ per cent. P_2O_5.

0.9517 gram gave 0.0994 gram $P_2O_7Mg_2 = 6.68$ per cent. P_2O_5.

The phosphorous acid was oxidised by bromine in presence of an excess of CO_3NaH. The analyses correspond most nearly to the formula

$$24MoO_3.4PO_3H_3.4(NH_4)_2O + 25Aq,$$
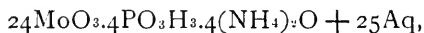
which requires :

		Calculated.	Found.
$24MoO_3$	3456	$77.80 \atop 7.38 \Big\} 85.18$	$77.45 \atop 7.71 \Big\} 85.16$
$4PO_3H_3$	328		
$4(NH_4)_2O$	208	$4.68 \atop 10.14 \Big\} 14.82$	$4.64 \atop 10.20 \Big\} 14.84$
$25H_2O$	450		
	4442	100.00	

The analyses confirm the formula first obtained, though the new salt contains eight molecules more of water of crystallisation.

ANTIMONOSO-TUNGSTATES.

When solutions of an acid tungstate of sodium are boiled with antimonious oxide, the latter very slowly dissolves, and it is difficult to obtain perfectly saturated solutions. It is best to employ antimonious oxide which has been freshly precipitated from the corresponding chloride by sodic carbonate and washed by decantation with cold water. If the precipitated oxide is allowed to stand for some time it becomes crystalline, and is then no longer available. The solution of antimonoso-tungstate obtained in this manner has a yellow color, and there is no sensible reduction of tungstic teroxide. Instead of this process the following may be employed with advantage. Freshly precipitated antimonious oxy-chloride, SbOCl, after washing with cold water, dissolves very readily in boiling solutions of alkaline tungstates of the meta-tungstic series. The solutions obtained in this way are also yellow. The oxychloride, on standing for some days, also becomes highly crystalline, and then dissolves with great difficulty. The solutions of sodic salts obtained as above become on evaporation thick and syrupy, and finally yield yellow gummy masses. There is in these cases also a tendency to supersaturation, as with the arsenoso-tungstates, though by no means to the same extent, and crystals of antimonious oxide (hydrate?) are sometimes deposited. The concentrated solution of the sodic salt obtained as above gives yellow oils with strong solutions of potassic or ammonic salts, which are but slightly soluble in a large excess of the latter. After pouring off the supernatant liquid, the oils may be redissolved in a small quantity of water, and again precipitated by a large excess of a concentrated solution of a potassic salt. I prefer for this purpose the bromide. Two or three repetitions of this process yield a nearly pure potassic antimonoso-tungstate, which may be advantageously used in the preparation of other salts. The alkaline salts of this series are either oily liquids or gummy masses with a pale yellow color, and very easily soluble. The solutions absorb oxygen rather slowly from the air, and are not easily oxidised by bromine or chlorine, unless in presence of an excess of alkali, as, for example, sodic bicarbonate. They then pass into antimonio-tungstates. The general formula of the antimonoso-tungstates is

$$m\text{WO}_3.n\text{Sb}_2\text{O}_3.p\text{R}_2\text{O}.$$
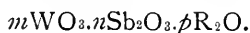
Analytical Methods.—The quantitative separation of antimony from tungsten in these compounds may be effected by the following methods. Hydric sulphide passed through the solution previously acidulated with chlorhydric acid precipitates antimonious sulphide completely, without any sensible reduction or precipitation of tungsten. An aliquot portion of the sulphide may then be heated in an atmosphere of dry carbonic dioxide, in the usual manner. This method applies to the greater number of cases. In its place we may often, but not always, employ the following, which usually gives good results in the cases of the alkaline salts. Potassic cyanide, as free as possible from carbonate and cyanate, is to be fused in a crucible of Berlin porcelain, and then allowed to cool. A weighed portion of the antimonoso-tungstate is then to be placed upon the fused mass, and the whole cautiously heated to low redness, and kept for a short time at this temperature. The antimony is completely reduced to metal, and after the solution of the alkaline salts in cold water, and washing at first with water and afterward with alcohol, may be weighed upon an asbestos filter. It will be seen that this process is the same as that devised many years ago by myself for the separation of tin from tungsten, worked out in my laboratory by Mr. F. H. Talbutt,[1] and known as Talbutt's method. The process unfortunately does not apply to cases in which insoluble compounds are formed together with the reduced metallic antimony. As a rule, when the process is successful, the antimony is finally in the form of large bright metallic globules, but in some cases it forms on reduction wholly or partially a black powder containing tungsten, and the method then fails. In these cases an accurate result may be obtained by mixing the salt or the potassic cyanide with a quantity of potassic or sodic carbonate sufficient to completely saturate both the tungstic and antimonic oxides present. This variation in the application of the method is due to my assistant, Mr. Herman Schmidt. In determining antimonious or antimonic oxides by this process, there is, of course, the disadvantage that a higher is always estimated from a lower molecular weight. The following analyses will serve to show the degree of accuracy which may be obtained under favorable circumstances, the method applying to antimonio-tungstates as well as to the antimonoso series. In an antimonio-tungstate of potassium not of definite constitution,

1.0924 gram gave 0.4407 gram metallic antimony $= 53.79$ per cent. Sb_2O_5.

1.0316 gram gave 0.4155 gram metallic antimony $= 53.71$ per cent. Sb_2O_5.

In another compound,

0.9059 gram gave 0.2251 gram metallic antimony $= 33.13$ per cent. Sb_2O_5.

1.0312 gram gave 0.2558 gram metallic antimony $= 33.08$ per cent. Sb_2O_5.

Antimonious oxide may also be determined in these compounds by titration with iodine, after adding to the solution an alkaline tartrate and an excess of sodic bicarbonate. It will be found advantageous to standardise the solution of iodine by means of pure crystallised antimonio-potassic tartrate—of course, after addition of an alkaline dicarbonate.

The determination of tungstic oxide may be effected by first separating the antimony as sulphide, and then precipitating the hot solution with baric chloride, after adding ammonia in small excess. The baric tungstate may be weighed upon an asbestos filter. It is better, however, to precipitate the tungstic oxide by means of mercurous nitrate; only, in case this method is to be applied, the antimony must be precipitated as sulphide after the addition of dilute sulphuric acid, and chlorhydric acid must not be employed.

11 : 3 *Baric Antimonoso-tungstate.*—A solution of sodic antimonoso-tungstate, obtained as above, gives with baric chloride a heavy pale yellow curdy or indistinctly crystalline precipitate. This salt melts under hot water to a thick yellow oily liquid, which dissolves very slowly, requiring a large quantity of water for solution. The solution has a yellow color and an acid reaction. It gives pale yellow flocky precipitates, with mercurous, argentic and thallous nitrates. Of this salt,

1.0722 gram lost on ignition with WO_4Na_2 0.0858 gram $= 8.00$ per cent.

1.3057 gram gave 0.3318 gram $Sb_2S_3 = 21.78$ per cent. Sb_2O_3.

1.3668 gram gave 0.3371 gram $Sb_2S_3 = 21.17$ per cent. Sb_2O_3.

1.2543 gram gave 0.1440 gram $SO_4Ba = 7.54$ per cent. BaO.

1.4895 gram gave 0.1709 gram $SO_4Ba = 7.53$ per cent. BaO.

1.9450 gram gave 1.6599 gram oxides $(WO_8 + Sb_2O_4) = 85.34$ per cent.

The analyses lead to the formula
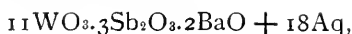
$$11WO_3.3Sb_2O_3.2BaO + 18Aq,$$

which requires:

		Calculated.	Found.		
$11WO_4$	2552	$\left.\begin{array}{c}63.07\\21.35\end{array}\right\}84.42$	62.79	$\left.\begin{array}{c}62.99\\21.78\end{array}\right\}84.37$	(diff.)
$3Sb_2O_3$	864		21.17		
$2BaO$	306	7.57	7:54	7.53	
$18H_2O$	324	8.00	8.00		
	4046	100.00			

The salt may be reduced to the type

$$6WO_3.Sb_2O_3.BaO + 9Aq,$$
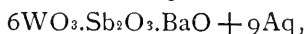
if we suppose Sb_2O_3 partially to replace WO_3; but in view of the very frequent recurrence of 22 molecules of tungstic oxide among complex inorganic acids, I am disposed to double the formula given above, and to write

$$22WO_3.6Sb_2O_3.4BaO + 36Aq.$$
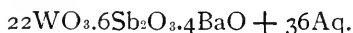
In the yellow oily salt obtained by precipitating sodic antimonoso-tungstate by means of potassic bromide, and carefully washing with a cold strong solution of the bromide, the ratio of the tungstic to the antimonious oxide was determined and found to be nearly $8WO_3$ to $2Sb_2O_3$, so that there is probably a series of antimonoso-tungstates with the general formula

$$8WO_3.2Sb_2O_3.nR_2O.$$

The quantity of solution taken gave 0.1091 gram $Sb_2S_3 = 0.0935$ gram Sb_2O_3, and 0.3417 gram $WO_3 = 71.51$ per cent. WO_3 and 21.49 per cent. Sb_2O_3.

ANTIMONOSO-MOLYBDATES.

The salts of this series are readily formed by boiling antimonious oxychloride, SbOCl, with an acid molybdate. The conditions are exactly the same as in the case of the corresponding antimonoso-tungstates. There is almost always a greater or less reduction of the molybdic oxide, and the solutions obtained have a greenish or greenish-blue tint, from the presence of Mo_2O_5 or a similar oxide. The ordinary acid ammonic molybdate of commerce in cold solution readily dissolves freshly precipitated antimonious oxide with only a slight reduction of the molybdic oxide; on boiling, much reduction takes place.

Analytical Methods.—Antimonious oxide cannot be separated from molybdic oxide by means of hydric sulphide, as a greater or less proportion of molybdic sulphide is always found. By proceeding in the manner already pointed out for the separation of antimony from tungsten, it is possible, in many cases at least, to separate antimony from molybdenum with a very satisfactory degree of accuracy. It will be found, however, always advantageous to add a quantity of potassic or sodic carbonate sufficient to neutralise both the molybdic and antimonious oxides before fusion with potassic cyanide. Crucibles of the best Berlin porcelain are alone adapted to fusions of this kind, and even when these are employed the action of the alkaline mixture upon the crucible must be taken into account. The best method is to add to the solution an alkaline tartrate, and then to render it alkaline with an excess of sodic bicarbonate. The antimonious oxide may then be determined by titration with iodine.

17 : 3 *Ammonic Antimonoso-molybdate.*—This salt crystallises from a solution of antimonious oxide in 14 : 6 ammonic molybdate, in pale greenish-yellow granular crystals, but its preparation is rather uncertain. It is insoluble in cold water : for analysis, the crystals were simply washed and dried upon woollen paper. In this salt,

0.7474 gram gave by titration with iodine 0.1618 gram Sb_2O_3 = 21.65 per cent.

0.5287 gram gave 0.0399 gram $(NH_4)_2O$ = 7.55 per cent.

1.0869 gram lost on ignition with MoO_4Na_2 and WO_4Na_2 0.1851 gram = 17.03 per cent.

The analyses lead to the formula

$$17MoO_3.3Sb_2O_3.6(NH_4)_2O + 21Aq,$$
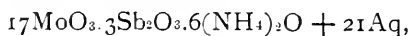
which requires :

		Calculated.	Found.
$17MoO_3$	2448	61.18	61.32
$3Sb_2O_3$	864	21.59	21.65
$6(NH_4)_2O$	312	7.79	7.55
$21H_2O$	378	9.44	9.48
	4002	100.00	

The molybdic oxide is estimated by difference. The solution from which this salt of ammonium separated gave, after twenty-

four hours, a fine yellow crystalline precipitate with manganous sulphate. The formula given may be reduced to the type

$$18MoO_3.2Sb_2O_3.6(NH_4)_2O + 21Aq,$$
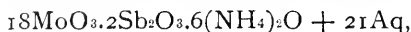
if we assume that one molecule of Sb_2O_3 plays the part of, or replaces, one molecule of molybdic oxide. In determining the water in this salt I employed a mixture of equal molecules of sodic tungstate and molybdate, which fuses at a temperature below that at which molybdic oxide is given off.

In formulating the arsenoso-tungstates and arsenoso-molybdates I have assumed provisionally that normal arsenites are represented by one or another of the three general formulas

$$As_2O_3.R_2O, \quad As_2O_3.2R_2O, \quad As_2O_3.3R_2O,$$
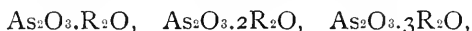
the three plumbic arsenites forming appropriate special instances. This view would establish a broad line of distinction between arsenites and phosphites, which last are now generally considered as hydryl-phosphinates, the general formula being

$$H.PO.(OH)_2.$$
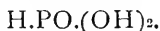
On the other hand, the existence of alkyl-arsinic acids appears to prove beyond a doubt that at least *some* arsenites belong to the same type with the phosphites. The older view must in any case be true for certain classes of salts, because the arsenites are not all reducible to the type $H.AsO.(OH)_2$, even if we admit that the atom of hydrogen is replaceable by an atom of univalent metal, for which there is no sufficient evidence in the case of the phosphites. If we consider the arsenic in the arsenoso-tungstates and arsenoso-molybdates which I have described to exist in the form of hydryl-arsinic acid, we shall have for the corresponding acids, respectively, the formulas

$$18WO_3 . 4[H.AsO.(OH)_2].8H_2O$$
$$16WO_3 .16[H.AsO.(OH)_2].9H_2O$$
$$8MoO_3. 4[H.AsO.(OH)_2].3H_2O$$
$$12MoO_3.10[H.AsO.(OH)_2].3H_2O$$
$$6MoO_3. 6[H.AsO.(OH)_2].3H_2O$$
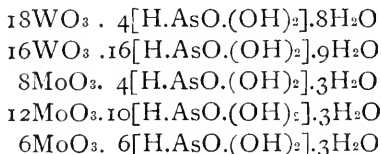
in which, of course, the basicity is purely arbitrary, since it depends in each case upon the number of molecules of base in a single salt. The internal basicity, as measured by the hydroxyl in the arsenical term, is always two, corresponding to one in the old style of writing. As the salts described appear to give off all their water when heated,

without other decomposition than loss from the volatilisation of arsenous oxide, it would seem to follow that their formulas must then at least be written as if they contained all the arsenic as As_2O_3, since

$$2[H.AsO.(OH)_2] = As_2O_3 + 3H_2O.$$
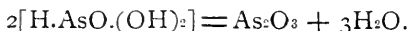
PHOSPHOROSO-PHOSPHO-TUNGSTATES.

24 : 1 : 2 : 5 *Potassic Phosphoroso-phospho-tungstate.*—When a solution containing both phosphorous and orthophosphoric acids is added to one of 12 : 5 sodic tungstate, no precipitate is formed, but on adding potassic bromide a white crystalline salt is thrown down, slightly soluble in cold water, but soluble in a large quantity of boiling water, forming a turbid liquid which has an acid reaction. The solution gives no precipitate with cupric sulphate, even on boiling and with or without free chlorhydric acid. It gives a white flocky precipitate with argentic nitrate, which becomes darker on boiling, and finally deep chocolate-brown. This reaction resembles that of the phospho-hypo-phospho-tungstates. The solution gives a very pale yellow indistinctly crystalline precipitate with mercurous nitrate, which is not reduced by boiling, and a white flocky precipitate with baric chloride. The salt dissolves with much difficulty in ammonia-water, but easily in solutions of alkaline carbonates. Chlorhydric acid gives a white precipitate in these solutions, readily soluble in ammonia. In this salt,

$\left\{\begin{array}{l} \text{1.5373 gram lost on ignition 0.0578 gram} = \text{3.76 per cent.} \\ \text{1.5373 gram gave 1.3702 gram mixed oxides} = \text{89.13 per cent.} \\ \quad WO_3 \text{ and } P_2O_5. \end{array}\right.$

1.7603 gram gave 0.1138 gram $P_2O_7Mg_2 = 4.13$ per cent. P_2O_5.

2.7325 grams gave 0.0836 gram $P_2O_7Mg_2 = 1.96$ per cent. P_2O_3.

In determining PO_3H_3 the solution in CO_3Na_2 was oxidised by bromine.

The analyses correspond with the formula

$$24WO_3.2PO_3H_3.P_2O_5.5K_2O + 13Aq,$$
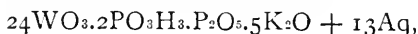
which requires :

		Calculated.		Found.	
$24WO_3$	5568	84.75		85.00	
P_2O_5	142	2.16	} 86.91	1.96	} 86.96
$2PO_3H_3$	164	2.49		2.50	
$5K_2O$	472	7.18		7.11	
$13H_2O$	224	3.41		3.43	
	6570	100.00			

25

When a solution of phosphorous and chlorhydric acids is mixed with one of the 24 : 1 phospho-tungstate of sodium,

$$24WO_3.P_2O_5.2Na_2O + 27Aq,$$
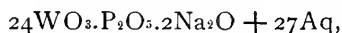
no precipitate is formed, but after a time relatively large colorless measurable crystals of the phospho-tungstate are deposited.

PHOSPHOROSO-PHOSPHO-MOLYBDATES.

72 : 3 : 2 : 9 *Ammonic Phosphoroso-phospho-molybdate.*—When the solution of phosphorous and chlorhydric acids obtained by treating phosphorous terchloride with cold water is mixed with a solution of 10 : 2 ammonic phospho-molybdate, a greenish-yellow crystalline precipitate is thrown down at once. The salt is very insoluble in water. It was washed upon the filter-pump and dried on woollen paper for analysis. In this salt,

1.0222 gram lost with WO_4Na_2 0.0975 gram $= 9.54$ per cent.

0.8936 gram gave 0.0354 gram $(NH_4)_2O = 3.96$ per cent.

1.1348 gram gave 0.0646 gram $P_2O_7Mg_2 = 3.63$ per cent.

1.2439 gram gave 0.0696 gram $P_2O_7Mg_2 = 3.58$ per cent.

The determination of phosphoric oxide was made after oxidation by bromine.

The analyses agree very well with the formula

$$72MoO_3.2PO_3H_3.3P_2O_5.9(NH_4)_2O + 38Aq,$$

which requires :

		Calculated.	Found.	
$72MoO_3$	10368	85.61	85.56	
$3P_2O_5$	426	3.52	3.58	3.63
$2PO_3H_3$	164	1.35	1.50	
$9(NH_4)_2O$	468	3.87	3.96	
$38H_2O$	684	5.65	5.58	
	12110	100.00		

The formation of this salt may be represented by the equation

$$3[24MoO_3.P_2O_5.3(NH_4)_2O] + 2PO_3H_3 =$$
$$72MoO_3.3P_2O_5.2PO_3H_3.9(NH_4)_2O.$$
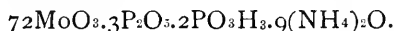
PHOSPHO-HYPOPHOSPHO-TUNGSTATES.

26 : 4 : 2 *Potassic Phospho-hypophospho-tungstate.*—When the 24 : 1 phospho-tungstate of sodium is boiled with an excess of a solution of hypophosphorous acid and a solution of potassic bromide is added to the clear pale blue filtrate, a white crystalline precipitate is after a time thrown down. The salt dissolves readily in hot water

to a clear solution. This gives a white flocky crystalline precipitate with baric chloride, a pale yellow precipitate with mercurous nitrate, and a white precipitate with argentic nitrate, which on boiling becomes first yellow, then brown, and finally takes a brownish color, and deposits a precipitate closely resembling ferric hydrate. Cuprous sulphate is without action on the solution. For analysis the freshly formed salt was thrown upon a filter, washed on the filter-pump thoroughly with cold water, and finally dried for analysis upon woollen paper. Of this preparation,

1.2162 gram gave 0.9706 gram mixed oxides $= 79.81$ per cent.
1.9865 gram gave 1.5903 gram mixed oxides $= 80.05$ per cent.
1.0921 gram gave 0.1408 gram $P_2O_7Mg_2 = 8.25$ per cent. P_2O_5.
1.5059 gram gave 0.1552 gram $P_2O_7Mg_2 = 6.59$ per cent. P_2O_5.
1.2162 gram gave 0.6340 gram $PtCl_6K_2 = 10.12$ per cent. K_2O.
0.9633 gram gave 0.5074 gram $PtCl_6K_2 = 10.22$ per cent. K_2O.
1.2705 gram lost with WO_4Na_2 0.1138 gram $= 8.96$ per cent.
0.8472 gram lost with WO_4Na_2 0.0778 gram $= 9.18$ per cent.

In the analyses the hypophosphorous acid was determined by oxidation with bromine, after adding an excess of sodic carbonate. The total phosphoric acid was then determined as ammonio-magnesic phosphate. In another portion of the salt the phosphoric acid proper was precipitated directly by magnesia-mixture in the usual manner. Corrections are of course made for the loss of hydrogen in ignition, according to the equation

$$2PO_2H_3 + H_2O = P_2O_5 + 8H,$$
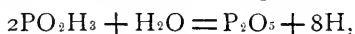
and also for the retention of one atom of oxygen by the mixed oxides, as shown by the same equation.

The analyses correspond to the formula

$$26WO_3.2PO_2H_3.4P_2O_5.9K_2O.Na_2O + 43Aq,$$

or

$$26WO_3.2[H_2.PO.OH].4P_2O_5.9K_2O.Na_2O + 43Aq,$$
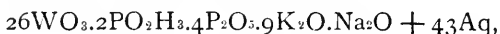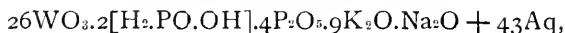
which requires:

		Calculated.	Found.	
$26WO_3$	6032	71.66	71.56	71.80
$4P_2O_5$	568	6.74	6.59	
$2PO_2H_3$	132	1.57	1.55	
$9K_2O$	850	10.09	10.12	10.22
Na_2O	62	0.74	0.78 (diff.)	
$43H_2O$	774	9.20	9.23	
	8418	100.00		

It cannot be doubted that similar compounds containing molybdenum in place of tungsten remain to be discovered. I did not, however, succeed in obtaining them by the action of hypophosphorous acid upon phospho-molybdates, and the precise conditions necessary are yet to be determined. It appears to be at least probable that classes of phosphoroso-hypophospho-tungstates and phosphoroso-hypophospho-molybdates will sooner or later be discovered.

ARSENOSO-PHOSPHO-TUNGSTATES.

The salts of this series are formed when solutions of orthophosphates and arsenoso-tungstates are mixed, and when arsenous oxide is boiled with a solution of an alkaline phospho-tungstate. The alkaline salts are sometimes crystalline and sometimes gummy. The series is probably a very extensive one.

Analytical Methods.—In these salts the arsenous oxide is best determined by titration with iodine after adding an excess of an alkaline dicarbonate. After separating arsenous oxide as sulphide by sulphydric acid, the phosphoric oxide may be determined by magnesia-mixture. Phosphoric and tungstic oxides may be determined together by mercurous nitrate and mercuric oxide after separating arsenous oxide from the solution as arsenous sulphide, dilute sulphuric acid being employed in place of chlorhydric acid. Water is best determined by heating over a radiator.

$32:14:3:10$ *Potassic Arsenoso-phospho-tungstate.*—This salt was prepared by boiling potassic phospho-tungstate with an excess of finely pulverised arsenous oxide. The filtered solution had a pale greenish-yellow tint, and after standing twenty-four hours deposited a mass of very minute greenish-yellow crystals. These were filtered off, washed with cold water, and then drained by the filter-pump. The drained mass was greenish-yellow, and packed into a gummy solid. The filtrate on evaporation gave a fresh quantity of the same salt, which is rather soluble in cold, and very easily soluble in hot water. Of this salt,

0.9333 gram lost by heating over a radiator 0.0398 gram $= 4.27$ per cent.

0.9333 gram gave 0.6094 gram $WO_3 + P_2O_5 = 65.29$ per cent.

1.0505 gram gave 0.2413 gram As_2O_3 with iodine $= 22.97$ per cent.

0.8456 gram gave 0.0472 gram $P_2O_7Mg_2 = 3.57$ per cent.

The analyses correspond fairly well with the formula

$$32WO_3.14As_2O_3.3P_2O_5.10K_2O + 28Aq,$$
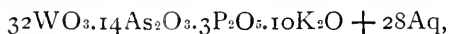
which requires :

		Calculated.	Found.
$32WO_3$	7424	61.51 ⎫	61.72 ⎫
$14As_2O_3$	2772	22.96 ⎬ 88.00	22.97 ⎬ 88.26
$3P_2O_5$	426	3.53 ⎭	3.57 ⎭
$10K_2O$	944	7.82	7.58
$28H_2O$	504	4.18	4.27
	12070	100.00	

12 : 2 : 2 : 6 *Sodio-potassic Arsenoso-phospho-tungstate.*—When sodic phospho-tungstate,

$$24WO_3.P_2O_5.2Na_2O + 27Aq,$$
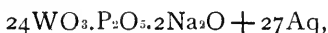
in solution, is boiled with arsenous oxide in excess, this last dissolves freely to a colorless or nearly colorless liquid. On adding ammonic chloride no precipitate is formed, but after acidulating with chlorhydric acid a white crystalline precipitate is thrown down. On standing, the supernatant liquid deposits very distinct pale yellow tabular crystals. When potassic bromide is added to the sodic solution, a yellow oil separates after a time, which dries to a pale yellow gummy transparent mass. Of this salt,

0.9284 gram lost over a radiator 0.0595 gram = 6.41 per cent.
0.9492 gram gave 0.0822 gram As_2O_3 with iodine = 8.65 per cent.
1.2191 gram gave 0.1061 gram As_2O_3 with iodine = 8.70 per cent.
0.8961 gram gave 0.0944 gram $P_2O_7Mg_2$ = 6.74 per cent. P_2O_5.
⎰ 0.8916 gram gave 0.6458 gram $P_2O_5 + WO_3$ = 72.43 per cent.
⎱ 0.8916 gram gave 0.5064 gram $PtCl_6K_2$ = 11.03 per cent. K_2O.

The formula which best represents the analyses is

$$12WO_3.2As_2O_3.2P_2O_5.5K_2O.Na_2O + 15Aq,$$
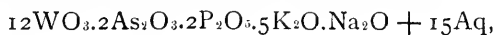
which requires :

		Calculated.	Found.	
$12WO_3$	2784	65.24	65.69	
$2As_2O_3$	396	9.28	8.65	8.70
$2P_2O_5$	284	6.65	6.74	
$5K_2O$	472	11.06	11.03	
Na_2O	62	1.45	1.48	
$15H_2O$	270	6.32	6.41	
	4268	100.00		

The arsenous oxide is too low, but the sum of the arsenous and tungstic oxides, as well as the percentages of the other constituents of the salts, agree well with the formula.

60 : 1 : 4 : 7 *Potassic Arsenoso-phospho-tungstate.*—When a solution of potassic phosphate is poured into one of sodic arsenoso-tungstate as prepared by boiling arsenous oxide with 12 : 5 sodic tungstate, no precipitate is formed ; but on adding chlorhydric acid the liquid becomes yellow, and, after standing, deposits beautiful pale yellow crystals. For analysis these were washed with cold water and dried on woollen paper. The salt is soluble in hot water, but appears to be decomposed by solution. In this salt,

1.2498 gram gave 0.0671 gram $P_2O_7Mg_2 = 3.43$ per cent. P_2O_5.
1.2587 gram gave 0.0151 gram As_2O_3 by iodine $= 1.20$ per cent.
1.0348 gram gave 0.9192 gram $WO_3 + P_2O_5 = 88.81$ per cent.
1.3143 gram lost over a radiator 0.0787 gram $= 5.99$ per cent. water.

The analyses correspond closely to the formula

$$60WO_3.As_2O_3.4P_2O_5.7K_2O + 55Aq,$$

which may also be written

$$60WO_3.2AsO_3H_3.4P_2O_5.7K_2O + 52Aq.$$
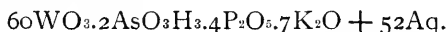
The formula requires :

		Calculated.	Found.
$60WO_3$	13920	85.21	85.38
$4P_2O_5$	568	3.48	3.43
As_2O_3	198	1.21	1.20
$7K_2O$	661	4.04	4.00 (diff.)
$55H_2O$	990	6.06	5.99
	16337	100.00	

It is of course very possible that this may be a double salt, but there are at present no data upon which we can base a rational distribution of the components.

ARSENOSO-ARSENIO-TUNGSTATES.

The salts which belong to this group are formed under the same conditions as the corresponding arsenoso-phospho-tung-states. They are in many cases highly crystalline and well defined, and appear to be very numerous.

Analytical Methods.—Arsenic acid may be directly determined in the soluble salts of this series by means of magnesia-mixture, but it is best to redissolve the precipitated ammonio-magnesic arsenate in chlorhydric acid, and precipitate a second time by ammonia. Arsenous oxide may be determined by titration with iodine after adding an excess of an alkaline dicarbonate. As a check upon the determination of the two oxides of arsenic, it is well to oxidise a portion of the salt directly by means of nitric acid, and then determine the total arsenic oxide by means of magnesia-mixture. A further check may also be obtained by reducing the arsenic oxide by boiling with sulphurous acid, and then titrating the total arsenous oxide by means of iodine. In solutions from which the arsenic has been completely removed as As_2S_3, tungsten can be determined by means of mercurous nitrate, provided that no chlorhydric acid or chloride is present.

21 : 1 : 4 : 10 *Potassic Arsenoso-arsenio-tungstate.*—When potassic bromide is added to a solution of arsenoso-tungstate of soda, and a solution of potassic arsenate, AsO_4K_2H, is then poured into the clear filtrate, a white crystalline precipitate is formed. This salt requires a very large quantity of hot water for solution. Baric chloride boiled with it gives a well-defined flocky-crystalline salt. Argentic nitrate gives a similar salt, but this has a faint tinge of fawn-color, perhaps due to the presence of a trace of potassic arsenate not completely removed by washing. Mercurous nitrate gives on boiling a clear yellow flocky-crystalline salt. In the potassic salt,

1.9985 gram gave 0.3468 gram $As_2O_7Mg_2 = 12.36$ per cent. As_2O_5.

2.0085 grams gave 0.0527 gram As_2O_3 by iodine $= 2.62$ per cent. As_2O_3.

After complete oxidation by nitric acid,

1.5004 gram gave 0.3162 gram $As_2O_7Mg_2 = 15.63$ per cent. As_2O_5.

1.9684 gram gave 1.2935 gram $WO_5 = 65.72$ per cent.

1.5825 gram gave 1.0346 gram $WO_3 = 65.37$ per cent.

1.3890 gram gave 0.9382 gram $PtCl_6K_2 = 13.09$ per cent. K_2O.

1.5765 gram lost over a radiator 0.0955 gram $= 6.06$ per cent.

The analyses lead to the formula

$$21WO_3.As_2O_5.4As_2O_5.10K_2O + 26Aq,$$

which requires :

		Calculated.	Found.
21WO	4872	65.86	65.72 65.37
As₂O₃ → As_2O_3 198	2.68	2.62	
4As₂O₅ → $4As_2O_5$ 920	12.43	12.36	
10K₂O → $10K_2O$ 940	12.70	13.09	
26H₂O → $26H_2O$ 468	6.33	6.06 6.39 (diff.)	
	7398	100.00	

Of course, in these salts, as in the arsenoso-phospho-tung-
states described, arsenic may be supposed to be in the form of
$[H.AsO.(OH)_2]$ either wholly or partially.

Classes of antimonoso-arsenio-tungstates, antimonoso-antimonio-
tungstates, and arsenoso-antimonio-tungstates, appear also to exist
and to be formed by processes exactly analogous to those described
in the cases of the compounds containing two oxides respectively
of the forms R_2O_3 and R'_2O_5, united with tungstic oxide.

(*To be continued.*)

SOME EXPERIMENTS ON THE QUANTITATIVE EFFICIENCY OF THE MARSH-BERZELIUS METHOD FOR THE DETECTION OF ARSENIC.

By W. P. Headden and B. Sadler, Jr.

We were led to make this investigation by the following obser-
vations : 1st. That when a solution containing a small quantity
of arsenic is brought into the evolution flask of a Marsh apparatus,
the evolution of arseniuretted hydrogen is copious and regular for
a short time, but it then diminishes very rapidly, and will often give
no mirror after the lapse of twenty minutes ; 2d. That when the
evolution is slow and regular, and the decomposition chambers are
together not less than three inches long, and that portion of the
tube in which the deposition of the arsenic is to take place is
sufficiently narrow and long, no arsenic escapes, either by being

carried forward and out of the tube mechanically, or in the form of arseniuretted hydrogen.

It is stated that in the detection of arsenic by means of Berzelius' modification of Marsh's method, enough arseniuretted hydrogen always escapes to give arsenic spots on porcelain. We find this to be true whenever the evolution of hydrogen is rapid, or the quantity of arseniuretted hydrogen is relatively very large, and the temperature of the decomposition chamber is not proportionately increased. If the evolution of hydrogen is too rapid, arseniuretted hydrogen, though present in relatively small quantities, may escape decomposition in chambers of the length given, even though they are kept at a dull red heat. We found it necessary in our experiments so to regulate the evolution of the hydrogen that it burnt with a flame not exceeding 5–6 mm. when issuing from an opening of about 1 mm. diameter.

Two grams of resublimed arsenious acid were dissolved in a sodic carbonate solution, and the solution diluted to 1 litre. The following determinations were made with this solution:

	Quantity of Sol. used.	Duration of the feeding.	Per cent. of As found.	Duration of Experiment.
1.	50 cc.	45 min.	98.80	2 hrs. 00 min.
2.	"	"	98.99	2 hrs. 30 min.
3.	"	"	98.56	4 hrs. 30 min.
4.	"	"	98.94	2 hrs. 30 min.
5.	"	55 min.	99.26	2 hrs. 30 min.

In experiment 3, the evolution of gas was so rapid and irregular at the beginning that a portion of the arseniuretted hydrogen escaped decomposition and was lost. The solution was fed through a burette, and the gas was dried by being passed over calcium chloride. In some experiments made previous to those recorded we used soda-lime as a dryer, with results varying from 91.60 per cent. to 94.30 per cent. of the arsenic present. The soda-lime was examined and found to contain arsenic. We attributed the low results to the action of the caustic alkali on the arseniureted hydrogen, and substituted pure calcium chloride for the soda-lime. In each of the five experiments given above we used a fresh portion of calcium chloride; because we noticed that when the same calcium chloride was used in more than one or two experiments, or until it had become coated with its aqueous solution, arseniureted hydrogen seemed to be retained, and our results correspondingly lowered.

In one series of experiments in which the same calcium chloride was used four times we obtained the following results : 1st. 98.94 per cent. ; 2d. 97.75 per cent. ; 3d. 96.36 per cent. ; 4th. 94.51 per cent. In two others in each of which the calcium chloride was used three times we obtained : 1st. 99.26 per cent. ; 2d. 98.70 per cent. ; 3d. 98.20 per cent. in one series, and, 1st. 98.94 per cent. ; 2d. 95.00 per cent. ; 3d. 94.70 per cent. in the other.

A very small drying tube was found to be sufficient. The one used was about 5 cm. long and rather more than 1 cm. in diameter.

In testing the applicability of this method to the determination of arsenic in minerals we selected an arseno-pyrite which had been analysed and found to contain 43.44 per cent. arsenic.

Two grams of this mineral were brought into solution by *aqua regia,* and the solution evaporated down with addition of sulphuric acid, and heated to expel the last traces of nitric acid. After this had been effected the solution was diluted to one litre, and two determinations of arsenic were made, with the following results : 32.15 per cent., 32.60 per cent. We attributed the low result—only 74.08 per cent. of the arsenic present—to the fact that the arsenic was present in the form of arsenic acid. One-half litre of the solution was taken and the arsenic acid reduced to arsenious by boiling with a solution of sulphurous acid. Four determinations were made with this solution, giving us 36.90 per cent., 37.55 per cent., 37.25 per cent. and 37.00 per cent. A subsequent determination, made from another sample treated in the same manner, gave 36.80 per cent. arsenic. The last solution differed from the solution of arsenious acid in that it contained a salt of iron. A measured portion of the solution precipitated with sulphuretted hydrogen, and a solution of arsenious acid prepared by dissolving the arsenic trisulphide in acid sodium sulphite, with subsequent addition of sulphuric acid, and boiling to expel all sulphur dioxide from the solution. Some of the sulphur and arsenic trisulphide which separated out did not redissolve in this solution; it was filtered off and brought into solution in another portion of acid sodium sulphite. The solutions were united and boiled with a slight excess of sulphuric acid. The solution remaining clear, it was supposed that all the polythionates had been destroyed, but the solution gave a precipitate of sulphur and arsenic trisulphide when brought into the evolution flask, and arsenic trisulphide was deposited in the tubes. The rest of the solution (200 cc.) was evaporated down

with the addition of sulphuric acid. It remained clear until it had been reduced to less than 50 cc., when a further separation of sulphur and arsenic trisulphide took place. The temperature of the solution was not determined. This precipitate was brought into solution and added to the main portion. Two determinations of the arsenic in this solution gave 41.67 per cent. and 41.53 per cent. arsenic. The arsenic was precipitated from the solution of another sample as the trisulphide, which was brought into solution in fuming nitric acid, evaporated down with sulphuric, and heated to expel last traces of the nitric acid, the arsenic acid reduced by solution of sulphurous acid, and the solution diluted up to 1 litre. Two determinations of the arsenic in this solution gave 41.55 per cent. and 41.52 per cent. of arsenic. We found no difficulty in reducing the arsenic acid in a sulphuric acid solution by means of a strong sulphurous acid solution, the reduction being completely effected within 1½ hours.

The next mineral experimented with was a tetrahedrite. The sample was brought into solution, the arsenic acid reduced and thrown down with the antimony and copper, the antimony and arsenic sulphides were dissolved out and separated by means of acid potassium sulphite. The arsenic was thrown down from this solution by sulphuretted hydrogen, and finally obtained in solution as arsenious acid. Two determinations of arsenic were made with this solution; one gave 4.20 per cent., the other 4.16 per cent. of arsenic.

A second sample was treated in the same manner, and two determinations made with this solution gave 3.81 per cent. and 3.81 per cent. The arsenic in a third portion of this solution was determined as magnesic-pyro-arsenate, and gave 3.801 per cent. of arsenic.

The zinc used was " C. P." bar zinc, but while it was free from arsenic, the amount of carbon contained in the different bars varied greatly, and only a few of them dissolved without any residue. The facts (1) that the presence of about 33 per cent. of iron in the arseno-pyrite reduced the amount of arsenic obtained by more than 10 per cent., (2) that our highest results were obtained with the purest zinc which we succeeded in procuring, (3) that when two experiments were made with the same bar of zinc, one-half of it being used in each, they agreed better than when they were made with different zincs, suggested that the constant deficit in our

determinations, even after we had eliminated other sources of error so far as we could, might be due to the influence, probably galvanic, of the carbon in the zinc. We endeavored to establish this by using some bar zinc which was very rich in carbon. The other conditions of the experiments were the same as in the first series given. The results obtained were 95.8 per cent., 95.2 per cent., 95.05 per cent. of the arsenic introduced into the flask. Another determination was made with the addition of copper sulphate solution, and we obtained 69.30 per cent. of the arsenic. In the early part of our investigation we brought, in some experiments, platinic chloride, in others a spiral of platinum wire, into the evolution flask, and obtained such low results that we rejected them.

In all of these experiments the arsenic was deposited in two tubes ; 97 per cent. on an average being deposited in the first tube, and all of the rest in the second. A third tube was used in a number of the experiments, but in no instance was any arsenic obtained in it.

The most convenient tube was found to be a hard glass tube with a total length of 18 cm. The decomposition chamber was 6 cm. long and 1 cm. wide. That portion in which the deposition took place was about 10 cm. long and 6 mm. wide. The second tube was of the same form, but the decomposition chamber need not be more than one-half so long.

Our conclusion is that the method will give satisfactory results under the following conditions :

1st. The zinc must be free from carbon, and pure in other respects.

2d. The arsenic should not be present in the form of arsenic acid.

3d. Iron, copper, platinum or their salts, and probably the other heavy metals and their salts, must be absent.

4th. The calcium chloride should be neutral and should not be used more than once.

5th. The feed and the evolution of the gas should both be slow and regular, and the decomposition chamber kept at a dull red heat.

XLVI.—ON THE ACTION OF CHROMIC SUPERFLUO-RIDE ON BENZOIC ACID.[1]

By C. Loring Jackson and George T. Hartshorn.

As the chromic superfluoride is instantly decomposed by water with the formation of chromic anhydride and hydrofluoric acid, we undertook the experiments described in the following paper in the hope that organic compounds containing hydroxyl would act in a similar way; and since Mallet's[2] determination of the vapor-density of hydrofluoric acid obliges us to assign it the formula H_2F_2, that thus we might obtain organic substances, in which the oxygen of the hydroxyl was replaced by two atoms of fluorine, as in fluosilicic acid. This hope has not been realized in the case of benzoic acid, with which we began our experiments, as the chromic superfluoride left the hydroxyl entirely unaltered ; but, on the other hand, it has led us to a very interesting result, as the products of the reaction were chromic fluoride (Cr_2F_6) and a difluorbenzoic acid, and therefore we have achieved for the first time, so far as we can find, the direct substitution of the hydrogen in an organic substance by fluorine. Preliminary experiments with acetic acid and benzol seem to show that the reaction is a general one,—in both cases the chromic superfluoride was reduced to a lower fluoride of chromium,—and there is good promise, there-fore, that it will prove of service in adding new members to the class of fluorine organic compounds, as yet so meagrely repre-sented.

We have not made a complete study of the difluorbenzoic acid, but have contented ourselves with doing enough to characterise it thoroughly, as we are anxious to avoid any interference with Paterno, who has already begun the investigation of organic bodies in which hydrogen is replaced by fluorine. Nor do we intend to continue our experiments on acetic acid and benzol, as Paterno has announced that he is at work on the fluorine derivatives of both these substances. We wish, however, to reserve for our future

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[1] From the Proceedings of the American Academy. Communicated by the Authors.
[2] This Journal **3**, 189.

study the action of chromic superfluoride on all other organic substances.

The remainder of the paper consists of the detailed account of our experimental work.

Action of Chromic Superfluoride on Benzoic Acid.

The chromic superfluoride was made by the action of 180 grams of fuming sulphuric acid on 60 grams of potassic dichromate and 100 grams of calcic fluoride, both of which must be perfectly dry. If the fuming sulphuric acid is very strong, it should be diluted with ordinary strong sulphuric acid, as, if this precaution is neglected, the action is so violent that it cannot be controlled, a large amount of the superfluoride is wasted, and in extreme cases the cover may be blown off the lead retort. The lead retort used was of the cylindrical form figured in most text-books for making the aqueous solution of hydrofluoric acid ; the fuming sulphuric acid was first introduced, the fluor-spar and potassic dichromate previously thoroughly mixed were then added, and stirred in with an iron rod, the cover put on, and the reaction started by a gentle heat. As soon as faint white fumes appear at the exit tube, the lamp should be removed, and, after the first violent evolution of gas has slackened, the action can be made to proceed smoothly by a gentle heat, although it is hard to avoid occasional rushes of gas. It is hardly necessary to say that the work should be carried on under a good hood, and the hands protected by india-rubber gloves. After the process is finished, the retort should be emptied before it has become cold, as after the residue has hardened its removal is both difficult and tedious.

The chromic superfluoride obtained in this way is not free from hydrofluoric acid, to judge from the white fumes which were observed mixed with the dark red heavy vapor ; but it was pure enough for our purpose, and was allowed to act directly on the solid benzoic acid, which was spread in a layer rather less than a centimeter thick over the bottom of a platinum dish, or on its cover ; for this purpose the lead pipe, which formed the exit tube of the retort, was brought down so that it nearly touched the surface of the acid. Absolute contact must be avoided, as in this case the tube soon becomes stopped up with the fused product. With a rapid stream of the superfluoride the action is vigorous,

the benzoic acid fusing and forming a black crust, which was made to spread over the whole surface by moving the dish when necessary; the crust was then removed,[1] and the same action repeated with fresh benzoic acid, until all the superfluoride was exhausted. In this way 180 grams of the crusts could be obtained in a single operation. If the stream of superfluoride was not rapid, the benzoic acid was apt to become covered with chromic anhydride, probably from a trace of moisture in the acid, and this not infrequently gave rise to unimportant deflagrations; but the amount of chromic anhydride formed even by this secondary reaction is very small, almost the whole of the chromic superfluoride being converted directly into the green chromic fluoride Cr_2F_6.

To obtain the difluorbenzoic acid from the crude product it was dissolved in a strong solution of sodic carbonate, and, after the chromic hydrate had been removed by filtration, fractionally precipitated with hydrochloric acid, the liquid being boiled with the separated benzoic acid after each precipitation. We found it wisest to divide the whole into two about equal fractions at first, and then to fraction the least acid portion again, when all the difluorbenzoic acid collected in the least acid fraction, which should be made very small; this was then boiled with water, and the residue purified by recrystallisation from boiling benzol and sublimation. The yield of difluorbenzoic acid is only 1.5 per cent. of the benzoic acid used.

Having obtained the difluorbenzoic acid, we next tried to detect the presence of monofluorbenzoic acid, and for this purpose examined the acid contained in the hot aqueous filtrate from boiling the difluor acid with water, and also the fraction immediately preceding the least acid one. As the metafluorbenzoic acid melts at $123°–124°$ according to Paterno and Oliveri,[2] the melting-point was of no assistance to us, and we have accordingly made a number of analyses of the barium salts of these fractions, both before and after a repetition of the fractional saturation, which have given results varying from 35.81 to 35.99 per cent. of barium; baric benzoate contains 36.15 per cent., baric fluorbenzoate 33.01 per cent.[3] We also thought it might be contained in a mixture of acids, obtained by boiling the crude product with insufficient

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[1] We think it right to mention that both of us were poisoned, one severely, by the crude product, which was spilt on our clothes in removing the crusts from the platinum dishes.

[2] Ber. d. ch. G. **15**, 1197.

[3] The most acid fractions were also pure benzoic acid, as was to be expected.

water, melting sometimes as low as 102° ; but this on fractional neutralisation was divided into difluorbenzoic acid and benzoic acid, as proved by analyses of the barium salt. We are convinced, therefore, that no monofluorbenzoic acid is formed by the action of chromic superfluoride on benzoic acid, but the products of the reaction are only difluorbenzoic acid and chromic fluoride with a little chromic anhydride as an impurity.

Difluorbenzoic Acid $C_6H_3F_2COOH$.

The acid prepared and purified, as described above, appears when sublimed in white flattened needles looking very much like benzoic acid, when crystallised from alcohol or benzol in short fine needles ; it sublimes at a temperature far below its melting-point, 232° (uncor.), but with much more difficulty than benzoic acid, and burns with a strongly green-bordered flame. It is essentially insoluble in cold water, and only slightly soluble in hot, the boiling solution depositing a few crystalline flocks of the acid on cooling ; not very freely soluble in cold alcohol or benzol, but freely in either of these solvents when hot, very soluble in ether or glacial acetic acid, less so in methyl alcohol, and almost insoluble in ligroine, or carbonic disulphide. Benzol is the best solvent for purifying it by crystallisation.

Its composition was established by the following combustions :

I. 0.2549 gram of substance burnt with plumbic chromate in a closed tube[1] gave 0.4964 gram of carbonic dioxide and 0.0982 gram of water.

II. 0.1595 gram gave 0.3131 gram of carbonic dioxide and 0.0506 gram of water.

	Calculated for $C_7H_4F_2O_2$.	I.	Found. II.
Carbon	53.16	53.13	53.52
Hydrogen	2.53	4.28	3.53

The ammonic difluorbenzoate is decomposed by evaporating its solution to dryness ; but a solution freed from ammonia by boiling gave white precipitates with plumbic acetate, and mercurous, mercuric and argentic nitrates, and a bluish white precipitate with cupric sulphate.

[1] We found it impossible to obtain agreeing results when the combustion was performed in the ordinary way with oxygen.

Baric Difluorbenzoate, $Ba(C_7H_3F_2O_2)_2$, made by boiling the acid with baric carbonate and water, crystallises in white scales, and contains no water of crystallisation even when only air-dried.

I. 0.2716 gram of the salt dried at 110° gave 0.1395 gram of baric sulphate.

II. 0.2674 gram gave 0.1378 gram of baric sulphate.

	Calculated for $Ba(C_7H_3F_2O_2)_2$.	Found. I.	II.
Barium	30.38	30.20	30.28

Its solubility in water was determined according to the method of Victor Meyer:

I. 1.5814 gram of a solution saturated at 15° gave 0.0188 gram of the salt by evaporation.

II. 2.6260 grams gave 0.0310 gram of the salt.

Therefore, the solution saturated at 15° contains the following percentages of the salt:

I.	II.
1.19	1.18

Calcic Difluorbenzoate, $Ca(C_7H_3F_2O_2)_2 . 3H_2O$.

This very characteristic salt, made by boiling the acid with calcic carbonate and water, begins to crystallise out, as soon as the liquid is somewhat concentrated, in bundles of silky needles, frequently a centimeter long, and slightly branched at a very acute angle.

I. 0.7886 gram of the air-dried salt lost 0.1058 gram at 100°.

II. 0.3605 gram lost 0.0495 gram.

	Calculated for $Ca(C_7H_3F_2O_2)_2.3H_2O$.	Found. I.	II.
Water	13.28	13.42	13.73

I. 0.2440 gram of the salt dried at 100° gave 0.0914 gram of calcic sulphate.

II. 0.3024 gram gave 0.1153 gram of calcic sulphate.

	Calculated for $Ca(C_7H_3F_2O_2)_2$.	Found. I.	II.
Calcium	11.30	11.02	11.21

Its solubility in water was determined according to the method of Victor Meyer:

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I. 2.0134 grams of a solution saturated at 15° gave 0.0100 gram of the anhydrous salt by evaporation.

II. 5.1731 grams gave 0.0256 gram of the anhydrous salt.

Therefore, the solution saturated at 15° contains the following percentages of the anhydrous salt :

| I. | II. |
| 0.50 | 0.49 |

The calcium salt when heated with an excess of lime gives off a combustible vapor, probably difluorbenzol, as only 4 per cent. of fluorine was removed from the acid in this way, but we do not intend to try to isolate this product for fear of interfering with Paterno. This observation was made in an attempt to determine the fluorine in the acid by Piria's method,[1] which showed that a much larger layer of alkali than could be obtained in this way was needed to remove the fluorine from the organic compound. We propose in our subsequent work to make another effort to solve this difficult problem in organic analysis.

It is to be observed that the large percentages of hydrogen obtained in the combustion of the acid correspond to the formula $C_6H_5F_2CO_2H$ better than to $C_6H_3F_2CO_2H$, and that our other analytical work is not capable of deciding between these formulas. The formula $C_6H_5F_2CO_2H$ would be that of an oxybenzoic acid containing two atoms of fluorine instead of one of oxygen $\left(\begin{smallmatrix} C_6H_4COOH \\ F_2H \end{smallmatrix}\right)$, and although the difficulty of removing the flourine from the acid rendered this formula highly improbable, we have thought it necessary to prove that it was incorrect. For this purpose we treated the acid with a large excess of potassic hydrate in alcoholic solution, and analysed the potassium salt, which can be precipitated by ether in broad silvery scales, when we obtained an amount of potassium corresponding to the formula $C_6H_3F_2CO_2K$.

[1] H. Schiff, Ann. Chem. **195**, 293.

NOTES ON THE EXTRACTION OF VANADIUM FROM MAGNETITE; ON THE CONDUCT OF SEVERAL COMPOUNDS OF VANADIUM TOWARDS REAGENTS; ON ITS QUANTITATIVE DETERMINATION; AND ITS SEPARATION FROM CHROMIUM.

By Edo Claassen.

1. By igniting finely pulverised and bolted magnetite with saltpetre (about ⅓ or ½ its weight) it is not decomposed. Even if this operation be repeated several times, until after extraction with hot water all the vanadium present is found in the filtrate the central part of the exceedingly minute grains of the ore is still magnetic, and has escaped oxidation.

2. If magnetite is digested for a long time with warm concentrated hydrochloric acid, it is in proportion to the purity of the ore more or less dissolved. The insoluble part then remaining is decomposed by igniting with saltpetre and soda. The mass taken from the crucible is mixed with the acid solution, from which most of the free hydrochloric acid has been previously evaporated. Some saltpetre is now added, and also, if necessary, some sodium carbonate, enough to give the acid solution a strongly alkaline reaction, after which the whole is evaporated to dryness, and kept red-hot for some time in an iron crucible. The contents of the crucible lixiviated with water furnish a liquid which contains *all* the vanadium (and also all the chromium) present in the ore, and from which it is separated as usual by barium chloride in form of barium vanadate.

3. Vanadium oxide, prepared by precipitating the green solution of vanadic acid in hydrochloric acid by ammonia, *cannot* be entirely dissolved in ammonium sulphide, even if the digestion with it is several times repeated.

4. Its solution is, however, easily effected by melting it in a covered porcelain crucible (if necessary, repeating this operation with the residue which sometimes remains after extraction with hot water) with six times its weight of equal parts of sulphur and sodium carbonate.

5. From the solutions thus obtained (see 3 and 4) it is impossible to precipitate in one operation all the vanadium by acetic, chlor-

hydric or sulphuric acid with or without the aid of heat. The bluish-green color of the filtrate is caused by some vanadium still present. If, however, the filtrate is neutralised or made alkaline and then mixed with ammonium sulphide and one of the above acids, some vanadium, but not all, is again precipitated as sulphide. By repeatedly (say six to ten times) operating in this way the vanadium is separated so far that only traces of it can be detected in the liquid (see 15).

6. Vanadium sulphide, ignited either with access of air for a long time, or after having been moistened with concentrated nitric acid or a solution of ammonium nitrate, leaves vanadic acid, but always mixed with some oxide. By extracting this residue with a solution of ammonium carbonate or with ammonia, the oxide is left undissolved.

7. Vanadium oxide, treated like the sulphide (see 6) leaves the vanadic acid also mixed with some oxide.

8. Ammonium vanadate, when ignited, leaves vanadic acid. This generally contains, however, a small quantity of oxide to be separated from the acid as above (see 6).

9. A colorless or faintly yellowish solution of ammonium vanadate turns yellow by being exposed to the air for some time. It has lost some ammonia, an addition of which will after heating restore the original color.

10. If vanadic acid is to be separated by means of ammonium chloride from a solution containing ammonium vanadate, care should be taken that this solution is colorless or nearly so, has a neutral or faintly alkaline reaction, or that if yellow, it be heated with some ammonia in order to get such a solution. For it should be remembered that in a yellow solution there will always be formed, besides the usual white or yellowish deposit, a yellow one, which, when being washed with a saturated ammonium chloride solution, will redissolve again with yellow color, thus causing a considerable loss of vanadic acid. For this reason a liquid containing the potassium or sodium salt should, after addition of ammonium chloride, not be allowed to stand in the open air much longer than necessary to precipitate all the ammonium vanadate. If the yellow deposit is formed, however, the liquid only needs heating with a little water and ammonia to make it fit for a new addition of ammonium chloride. If a chromate, however, is present in the solution together with a vanadate, it is evident that the liquid

will always be more or less yellow, even when having an alkaline reaction.   In this case notice has to be taken of the alkaline reaction only, which suffices to indicate that the solution is fit for an addition of ammonium chloride.

11. Although the use of ammonium chloride is frequently recommended as a means of exactly determining the quantity of vanadic acid present, it seemed to me, as some vanadic acid was occasionally found in the filtrate, to be well worth while to make some experiments on this subject.   These indicated positively that a small amount of the vanadate always enters the filtrate, from which it can be separated by alcohol.   On redissolving this precipitate in a little water and adding some ammonium chloride, almost all the vanadate is separated, so that only traces are lost.

12. All vanadic acid present in a neutral solution can be separated by means of lead acetate.   The lead vanadate formed can be perfectly decomposed by digestion with a mixture of chlorhydric acid and alcohol.   The filtrate from the lead chloride formed is entirely free from lead when a sufficient quantity of alcohol is added. After the distillation of the alcohol and the evaporation of the residue in a platinum dish with addition of some concentrated sulphuric acid to dryness, there remains after ignition, all the vanadic acid present, mixed, however, with some oxide.   Instead of decomposing the precipitate in this way, the method described under 19 can often be used with advantage.

13. From neutral solutions of the vanadates all vanadic acid is precipitated also by barium chloride.   By boiling the precipitate of barium vanadate with dilute sulphuric acid it *cannot be entirely decomposed.*   By mixing the dry precipitate with some potassium bisulphate and igniting, decomposition takes place so perfectly that after extraction with water not a trace of vanadic acid is left with the residue of barium sulphate.   The solution obtained may be precipitated with a small excess of lead acetate, and the lead vanadate formed (besides lead sulphate) be decomposed as described under 12.

14. If a mixture of barium vanadate and barium sulphate is digested with hydrochloric acid, or with a mixture of the latter and alcohol, a considerable part of the vanadium will enter the bluish-green solution, while some will be retained in the residue on the filter.   Treatment with concentrated nitric acid seems to have no effect on this residue.

15. It has been recommended for the quantitative determination of vanadium to precipitate it from a solution of the chloride, previously saturated and reduced by sulphuretted hydrogen gas, by an addition of mercuric chloride and ammonia. Experiments made in this way gave bad results, as even by repeated precipitation it was possible to separate but a small portion of the vanadium from the solution.

Experiment 1.—0.086 gram of vanadic acid was dissolved in concentrated hydrochloric acid, the solution diluted, saturated with sulphuretted hydrogen gas, and mixed with a small excess of the above reagents. The precipitate contained but 0.007 gram of vanadic acid. The same operation twice repeated furnished an equal amount, so that out of the 0.086 gram taken, 0.014 gram only went into the three precipitates, while the balance, 0.072 gram, remained dissolved in the filtrate.

Experiment 2.—Another quantity of vanadic acid was dissolved in hydrochloric acid, and treated, etc., as above. The first precipitate furnished 0.006 gram of vanadic acid only, while the two next ones gave 0.150 gram. Some vanadium still remained in the filtrate; it was repeatedly precipitated as sulphide (see above under 5). The three first precipitates gave 0.052 gram of vanadic acid, and the four next ones 0.014 gram (all, however, containing some oxide), while the filtrate now contained but a very small amount of vanadium—hardly more than a trace.

16. Vanadic acid or oxide, melted with soda and saltpetre, produces a colorless mass which, with water, gives a colorless solution. If, however, chromic oxide, even in small quantity, is present, the color of the melted mass is more or less yellow, according to the quantity of the oxide, as is also that of the solution of the mass.

17. In consequence of the fact that from the solution of an alkaline vanadate not the total amount of vanadic acid is separated by ammonium chloride, an exact quantitative determination by one operation is impossible in this way (see 11). The balance remaining in the filtrate, if not separated as described in 11), will evidently, if chromium oxide is also present, increase the weight of the chromium precipitate separated afterwards.

18. From a mixture of vanadic acid and chromium oxide concentrated hydrochloric acid will by digestion extract the greater part of the vanadic acid, while traces only of chromium oxide

enter the solution.   At one trial 0.083 gram of such a vanadic acid
left after digestion 0.030 gram, from which, after having been
moistened with concentrated nitric acid and ignited by a repeated
digestion with hydrochloric acid, but 0.001 gram was extracted.
The undissolved 0.029 gram was then melted with soda and
sulphur (see 4), by which operation 0.010 gram more of vanadic
acid was separated, so that the treatment with concentrated
hydrochloric acid left 15.64 per cent. of the vanadic acid with the
chromium oxide.   It was, however, stated that the original mixture
of vanadic acid and chromium oxide contained also some vanadium
oxide.   On account of this fact there seems to be the possibility
that all the undissolved 15.64 per cent. were solely due to the
vanadium oxide, in which case concentrated hydrochloric acid
would certainly furnish a good means of separating vanadic acid
from chromium oxide.   Further experiments made on this matter
would without doubt be well worth trying.

19. If a mixture of vanadic acid or oxide and chromium oxide
is melted with six times its weight of soda and sulphur in a
covered porcelain crucible (which operation may be once repeated,
if there is a remnant on the filter after extraction with water), and
the melted mass treated with hot water, all the vanadium present
is found in the solution, while all the chromium remains on the
filter as oxide.   The solution of the sulphovanadate is heated in a
covered beaker glass for a longer time with a small excess of
nitric acid ; then some soda is added to make the reaction alkaline
and the heating continued until the evolution of carbonic acid gas
has ceased.   The contents of the beaker are now brought into a wide
porcelain or platinum crucible, evaporated to perfect dryness and
melted.   The melted mass is lixiviated with hot water, the solution
carefully neutralised with acetic acid, and then precipitated with
lead acetate.   The washed precipitate suspended in water, con-
taining some nitric acid, is decomposed by sulphuretted hydro-
gen gas, and the filtrate now obtained furnishes after evaporation
and ignition all the vanadic acid present.

NOTES.

Valence of Phosphorus.

Evidence serving to throw light upon the question of the true valence of phosphorus, as well as of other members of the nitrogen group, is of such a character that a well-defined difference of opinion upon it has existed among chemists, one class regarding these elements as trivalent and another as quinquivalent. The former class account for the existence of such substances as phosphorus pentachloride by holding that they are examples of the so-called molecular compounds, *i. e.* that phosphorus pentachloride is the result of combination between a molecule of phosphorus trichloride and one of chlorine; while the latter class admit the existence of unsaturated compounds, of which ammonia, phosphoretted hydrogen and phosphorus trichloride are examples.

The idea of molecular combination in the case of phosphorus pentachloride, for example, is supported by the fact that this substance, when vaporised by itself, shows a density required by a mixture of an equal number of molecules of phosphorus trichloride and chlorine. On the other hand, Würtz has shown that phosphorus pentachloride may be vaporised without decomposition in an atmosphere of phosphorus trichloride. Furthermore, the discovery by Thorpe of phosphorus pentafluoride, a compound stable in the gaseous state, points also to the quinquivalent nature of phosphorus; against this, on the other hand, it has been argued that this substance is merely a stable molecular compound.

The recent investigations of Michaelis and La Coste[1] contribute evidence very decidedly in favor of the quinquivalence of phosphorus.

Were it possible to obtain a compound isomeric with phosphorus oxychloride, and to prove by its method of preparation and properties that its constitution is represented by the formula $Cl_2 = POCl$, in which one of the chlorine atoms is united to phosphorus through the intervention of oxygen, then a decision in favor of the quinquivalence of phosphorus might safely be rendered. Compounds analogous to phosphorus oxychloride and its hypothetical isomer, in which the chlorine atoms of the latter are replaced by phenyl groups, have been prepared and described.[2] One of these, triphenylphosphine oxide, $PO(C_6H_5)_3$, is formed from triphenylphosphine dibromide, and also from triphenylphosphine by processes perfectly analogous to those involved in the production of phosphorus oxychloride from phosphorus penta-

[1] Berichte der deutschen chemischen Gesellschaft **18**, 2118.
[2] *Ibid.* **15**, 803; Annalen der Chemie **229**, 305.

chloride on the one hand, and from phosphorus trichloride on the other ; this analogy is made apparent by the following scheme:

Phosphorus pentachloride.   Phosphorus oxychloride.   Phosphorus trichloride.

$$P{<}{Cl_3 \atop Cl_2} \quad \dashrightarrow \quad P{<}{Cl_3 \atop O} \quad \longleftarrow \quad PCl_3$$

Triphenylphosphorus dibromide.   Triphenylphosphine oxide.   Triphenyl-phosphine.

$$P{<}{(C_6H_5)_3 \atop Br_2} \quad \quad P{<}{(C_6H_5)_3 \atop O} \quad < \quad P(C_6H_5)_5.$$
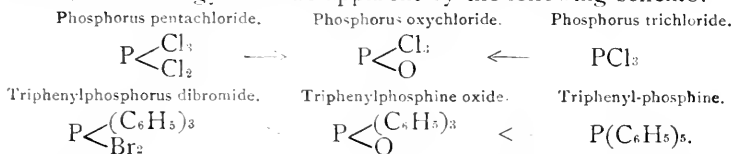
The other compound of the empirical formula, $PO(C_6H_5)_3$, was formed by treating diphenylphosphorus chloride with phenol, thus :

$$(C_6H_5)_2PCl + C_6H_5OH = HCl + (C_6H_5)_2POC_6H_5.$$
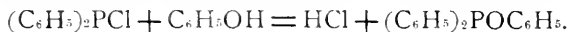
This compound is called phenoxyl-diphenyl phosphine. The first of these compounds, triphenylphosphine oxide. is a solid, melting at $153.5°$ C., and is perfectly indifferent toward bromine, oxygen, sulphur, selenium, benzyl chloride and methyl iodide ; while the second, phenoxyl-diphenyl phosphine, isomeric with the first, is a thick oily liquid and readily combines directly with all the above-mentioned elements, and, more than that, forms crystalline addition products with the halogen compounds of the alkalies, thus showing an analogy with the substitution products of phosphoretted hydrogen, or, in other words, possessing the properties of a compound of trivalent phosphorus. The constitution of this second compound can then only be expressed by representing it as a derivative of the hypothetical isomer, $P{<}{Cl_2 \atop OCl}$ of phosphorus oxychloride.

As a result, therefore, of the study of these two isomeric substances, their methods of formation and their chemical conduct, the conclusion is drawn that phosphorus, and consequently all the other members of the nitrogen group, are to be regarded as quinquivalent, and that all such compounds as correspond to phosphorus trichloride, etc., are to be considered as unsaturated.

W. C. D.

On the Qualitative Detection of Mercuric Compounds.

In the ordinary course of qualitative analysis the black residue of sulphides, from which As, Sb and Sn sulphides have been extracted by NaOH or K_2S, are boiled with dilute HNO_3, when HgS is said to remain behind as a black insoluble residue. In point of fact, instead of being black, this residue may be brown, dark yellow, light yellow or white, according to circumstances, even though it contains Hg, as it should. All I can say definitely of this compound is that it always contains sulphur and also nitric acid, and probably consists of a mixture of HgS and $Hg(NO_3)_2$. There is at least one compound of this kind known, and accordingly it would seem that the formation of some such compound

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might be anticipated in such a process as that given above ; but it is not noticed in any text-book on qualitative analysis so far as I know. Fresenius states under the reactions for Hg that *concentrated* HNO_3 forms a compound whose formula is $2HgS.Hg$ $(NO_4)_2$, but it certainly appears from my own experiments that compounds of the same kind, but varying composition, are formed on boiling with *dilute* HNO_3, especially if the boiling be protracted. No way is suggested in Fresenius or any other book for deciding whether a yellow or white residue contains HgS, and the pupil will ordinarily think it not worth while to test by the dry way unless the residue is black, as it is advertised to be. A student in my laboratory has accidentally discovered that boiling this yellow or white residue with Na_2CO_3 solution, after careful washing with water, restores the black color. Just how the composition of the residue is changed by this treatment I have not yet ascertained, but the resulting product is dense, jet black and heavy, and probably contains considerable HgS. The nature of this change needs further investigation.   J. TORREY.

The First Work in Pure Chemistry in America.

In a paper by HUGO SCHIFF and R. SESTINI, of Florence, Italy, which recently appeared in the *Annalen der Chemie* (Band 228, S. 72), occurs the following passage which will be of interest to American chemists :

" A compound of arsenious acid with potassium iodide was first described in the year 1830 by J. P. Emmett. He obtained the compound in the form of a white crystalline powder, by adding potassium iodide to very dilute solutions of arsenious acid or potassium arsenite exactly neutralised with acetic acid." . . . .

" The compound has a two-fold interest from the historical standpoint. John Patton Emmett, Professor in the University of Virginia, from its foundation (1825 to 1842), was one of the first teachers of chemistry in the Union. With the exception of a few investigations by Robert Hare and the elder B. Silliman, which pertained rather to analytical, technical and mineralogical subjects, the communication of Emmett belongs to the earliest period of chemistry in North America, where the science has since grown up to a strong, independent life.

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ON BENZOYLACETIC ACID AND SOME OF ITS DERIVATIVES. PART III.[1]

By W. H. PERKIN, Jun., *Privatdocent at the University of Munich.*

In the first two parts of this research I described a number of simpler derivatives of ethylic benzoylacetate, showing it to be analogous to ethylic acetoacetate in almost every respect. In the third part I wish to give an account of some of the more complicated reactions into which this body enters, namely, the preparation and properties of ethylic dibenzoylsuccinate, ethylic monobenzoylsuccinate, and dehydrobenzoylacetic acid.

Ethylic Dibenzoylsuccinate.

By the action of iodine on the sodium compound of ethylic acetoacetate, Harrow[2] obtained ethylic diacetylsuccinate, according to the equation:

$$\begin{array}{l} CH_3.CO.CHNa.COOEt \\ CH_3.CO.CHNa.COOEt \end{array} + I_2 = \begin{array}{l} CH_3.CO.CH.COOEt \\ CH_3.CO.CH.COOEt \end{array} + 2NaI.$$
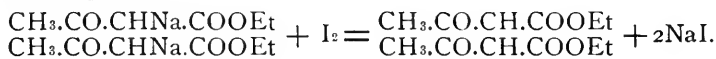
On boiling this compound with dilute sulphuric acid it is partly hydrolysed, giving off one molecule of alcohol, and forming the ethylic salt of carbopyrotritaric acid, thus:

$$C_{12}H_{18}O_6 = C_{10}H_{12}O_5 + C_2H_5.OH.$$
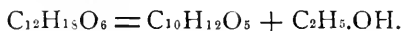
If the saponifying action is continued further, this ethereal salt is split up into carbopyrotritaric acid and alcohol:

$$C_{10}H_{12}O_5 + H_2O = C_8H_8O_5 + C_2H_5.OH.$$
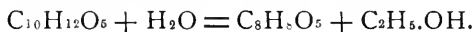
[1] Communicated by the Author.   [2] Trans. 1878, 425.

This acid, which Harrow supposes to have the constitution:

$$CH_3.CO \atop COOH \!\!\!>\!\! CH.CH\!\!<\!\! {C(CH) \atop -CO}\!\!>\!\!O,$$

is resolved, on further heating with dilute sulphuric acid, into pyrotritaric acid and carbonic anhydride, thus:

$$C_8H_8O_5 = C_7H_8O_3 + CO_2.$$
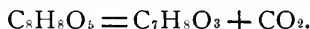
On account of this latter reaction, Harrow assigns the following constitution to pyrotritaric acid:

$$CH_3.CO.CH(COOH).CH : C : CH_2.$$

Considering the complicated nature of these reactions, it appeared to be interesting to repeat them with ethylic benzoylacetate, in order to determine whether similar compounds would be produced, corresponding with carbopyrotritaric and pyrotritaric acids.

It was necessary, in the first place, to prepare ethylic dibenzoylsuccinate, which can easily be effected by a method analogous to that employed by Harrow for preparing ethylic diacetylsuccinate, namely, by the action of iodine on ethylic benzoylsodacetate. 4.7 grams of the finely powdered sodium compound were mixed with dry ether, and 2.8 grams of iodine added in small quantities at a time, the whole being well shaken and cooled after each addition. At first the color of the iodine disappears instantly, but towards the end of the reaction much more slowly, the mixture becoming slightly brownish.

The ethereal solution is filtered from the precipitated sodic iodide, washed with water and a little sulphurous acid in order to remove any slight excess of iodine, and then dried over calcium chloride. On distilling off the ether, a brownish mass remains, which becomes almost entirely solid when exposed for about 24 hours over sulphuric acid in a vacuum. These crystals are spread out on a porous plate, in order to remove as much of the motherliquor as possible, washed on a filter, with small quantities of ether, until an almost colorless mass remains behind, and purified by two crystallisations from alcohol.

0.1630 gram substance gave 0.0890 gram H_2O and 0.4113 CO_2.

	Found.	Theory, $C_{22}H_{22}O_6$.
C	68.82 per cent.	69.11 per cent.
H	6.06	5.76
O	25.12	25.13

The compound is therefore ethylic dibenzoylsuccinate, formed according to the equation:

$$C_6H_5.CO.CHNa.COOEt \atop C_6H_5.CO.CHNa.COOEt + I_2 = {C_6H_5.CO.CH.COOEt \atop C_6H_5.CO.CH.COOEt} + 2NaI.$$
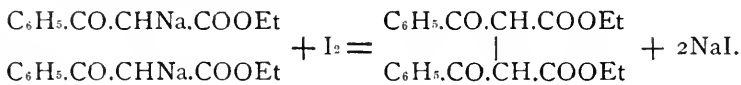
Ethylic dibenzoylsuccinate melts at 128–130°, and when heated in a test tube it is decomposed, a carbonaceous residue being left. It is sparingly soluble in cold alcohol, but easily in hot, being deposited from this solution on cooling in short thick prisms; it may be obtained perfectly colorless by repeated recrystallisation. It is easily soluble in ether and benzene, crystallising in small needles on evaporation.

The behavior of ethylic dibenzoylsuccinate with concentrated sulphuric acid is very characteristic. The finely powdered substance dissolves in the acid, forming an almost colorless solution, and on adding water is reprecipitated, apparently unchanged. When the solution is heated it becomes first reddish and then olive-green, but if the heating is continued the color changes to a bluish-red. If this solution when cold is poured into a little water, a brownish liquid is obtained, with a strong blue fluorescence; an excess of water destroys the coloration altogether. As ethylic benzoylsuccinate contains two CH groups which are each joined on both sides to carbonyl groups, it appeared very probable that it might yield a disodium compound on treatment with sodium ethoxide, according to the equation:

$$C_6H_5.CO.CH.COOEt \atop C_6H_5.CO.CH.COOEt + 2NaOEt = {C_6H_5.CO.CNa.COOEt \atop C_6H_5.CO.CNa.COOEt} + 2EtOH.$$
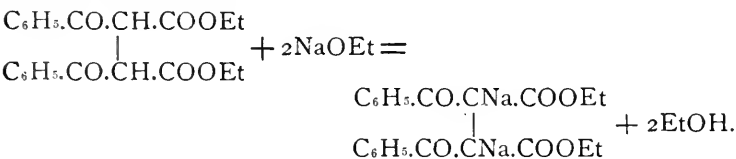
This was in reality found to be the case, the compound being best formed in the following way: 0.3 gram of sodium is dissolved in the smallest possible quantity of alcohol, and while still warm an excess of pure dry ether is added, the whole being thoroughly mixed, by means of a glass rod, until the liquid becomes clear, or only slightly turbid. An ethereal solution of 2.5 grams of ethylic dibenzoylsuccinate is then added, and the whole allowed to stand for some time. The sodium compound slowly separates out as a slightly yellowish mass, and as soon as the precipitation is finished

it is collected by means of a vacuum pump, and well washed, first with a mixture of alcohol and ether, and lastly with ether, in which the compound is almost insoluble. The disodium compound was thus obtained as an almost colorless mass, which, after standing for some hours over sulphuric acid in a vacuum, gave the following numbers on analysis:

0.4434 gram substance gave 0.1575 Na_2SO_4.

	Found.	Theory.
Na	11.49 per cent.	10.80 per cent.

When perfectly dry this compound is fairly stable, but if it contains a little alcohol it quickly takes up moisture from the air and is decomposed. It is fairly soluble in hot alcohol, sparingly in the cold. On adding a drop of ferric chloride to the alcoholic solution, a dirty red coloration is formed. Cupric acetate precipitates the copper salt as a light-green amorphous mass. The sodium compound is easily decomposed by dilute acids, the original substance being apparantly regenerated.

If this compound is treated with an ethereal solution of iodine, sodium iodide is instantly precipitated, and on filtering and evaporating the ethereal solution a thick brownish oil is obtained, which is probably ethylic dibenzoylfumarate, produced according to the equation:

$$C_6H_5.CO.CNa.COOEt \atop C_6H_5.CO.CNa.COOEt + I_2 = {C_6H_5.CO.C.COOEt \atop \| \atop C_6H_5.CO.C.COOEt} + 2NaI.$$
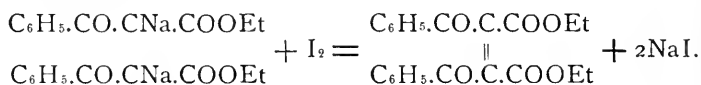
The oil, unfortunately, would not crystallise, and therefore a good analysis could not be obtained. The solution in chloroform, however, decolorised bromine instantly, without evolution of hydrobromic acid, showing that it is an unsaturated compound.

Decomposition Products of Ethylic Dibenzoylsuccinate.

On mixing ethylic dibenzoylsuccinate with alcoholic potash it dissolves, producing an intense yellow solution. If after allowing it to remain for some time, or gently warming, the product be acidulated with dilute sulphuric acid, a yellow amorphous acid is precipitated; unfortunately, however, this could not be obtained in a crystalline state, as it is extremely soluble in all solvents except water. In order to purify it as far as possible it was dissolved in ammonia, and fractionally precipitated with dilute acid;

this treatment having been repeated several times, the product was finally converted into the silver salt, and analysed with the following result:

0.3047 gram substance gave 0.1171 gram Ag.

	Found.	Theory, $Ag_2C_{18}H_{12}O_6$.
Ag	38.43 per cent.	40.00 per cent.

Although these numbers do not agree very closely with theory, it is yet probable that the substance is in reality impure dibenzoyl-succinic acid. On adding ferric chloride to the solution of the acid in alcohol, or that of the ammonium salt, a peculiar dark-green precipitate is formed, closely resembling that obtained with sulphuric acid.

The acid dissolves in concentrated sulphuric acid, producing a yellowish solution which becomes of a beautiful crimson on warming. The acid gives acetophenone when distilled with soda-lime. From the above experiments it appeared unlikely that better results would be obtained by saponifying with other alkalis, such as baryta-water, and it was thought probable that, as in the case of ethylic diacetylsuccinate, dilute acids might be employed with greater advantage. The following method of hydrolysis was finally adopted.

Pure ethylic dibenzoylsuccinate was boiled with an excess of dilute sulphuric acid (1 : 2) for about six hours in a flask connected with a reflux condenser, at the end of which a test-tube containing baryta-water was fixed. The mass became more and more darkly colored, but very little carbonic anhydride was given off. When cold, the product was collected, washed with water, well shaken with a warm solution of sodic carbonate, and filtered. The residual tarry mass was then washed with water, again boiled with dilute sulphuric acid for six hours, and the extraction with sodic carbonate repeated as before. The greater part dissolved, leaving a thick black residue, from which mere traces of an organic acid were obtained on repeating the treatment with sulphuric acid.

The different alkaline solutions were mixed and acidified with dilute sulphuric acid. This produced a precipitate which, after being recrystallised several times from dilute acetic acid (70 per cent.), was obtained pure in the form of small colorless needles which gave the following numbers on analysis:

I. 0.1862 gram substance gave 0.0664 H_2O and 0.4752 CO_2.

II. 0.2032 gram substance gave 0.0745 H_2O and 0.5249 CO_2.

III. 0.1627 gram substance gave 0.0592 H_2O and 0.4167 CO_2.

	Found.				Theory, $C_{18}H_{12}O_5$.
	I.	II.	III.		
C	69.60	70.42	69.85	per cent.	70.13 per cent.
H	3.96	4.07	4.04		3.89
O	26.44	25.51	26.11		25.97

The formula of this acid is therefore $C_{18}H_{12}O_5$, and it is formed from ethylic dibenzoylsuccinate by the removal of 2 mols. of alcohol, thus :

$$\underset{\substack{\text{Ethylic dibenzoyl-}\\ \text{succinate.}}}{C_{22}H_{22}O_6} + H_2O = \underset{\text{New acid.}}{C_{18}H_{12}O_5} + 2C_2H_5.OH,$$
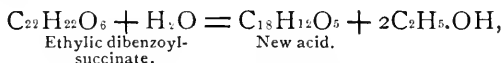
its formation corresponding precisely with that of carbopyrotritaric acid from ethylic diacetylsuccinate :

$$C_{12}H_{18}O_6 + H_2O = C_8H_8O_5 + 2C_2H_5.OH.$$

This new acid melts at 236–238°. It is easily soluble in ether, alcohol, benzene, light petroleum, and glacial acetic acid, less so in a 70 per cent. solution of the latter solvent, from which it crystallises in small needles. The alcoholic solution gives an orange coloration with ferric chloride.

This acid, $C_{18}H_{12}O_5$, dissolves in concentrated sulphuric acid, forming a colorless solution, which, however, acquires a beautiful violet color when warmed. Heated by itself in a test-tube, it first melts and then sublimes, water being given off at the same time. The sublimate is crystalline, but apparently insoluble in ammonia, and is perhaps the anhydride of the acid. The acid $C_{18}H_{12}O_5$ is easily decomposed on distilling it with soda-lime, acetophenone being formed. Its alcoholic solution does not appear to react with phenylhydrazine or hydroxylamine. It is, however, a strong acid, dissolving easily in ammonia, sodic hydroxide, or sodic carbonate solutions. The ammonium salt was prepared by dissolving the acid in ammonia and then allowing the solution to stand over sulphuric acid in a vacuum until the excess of alkali had evaporated. On adding silver nitrate to this solution, a white precipitate of the silver salt was formed ; this, when dried over sulphuric acid in a vacuum, gave the following numbers on analysis :

0.4817 gram substance gave 0.1939 gram silver.

	Found.	Theory.	
		$C_{18}H_{10}O_5Ag_2$.	$C_{18}H_{12}O_6Ag_2$.
Ag	40.25 per cent.	41.29 per cent.	40.00 per cent.

This result not being satisfactory, a complete analysis of the silver salt was made with the following result:

0.2683 gram substance gave 0.400 CO_2, 0.0562 H_2O and 0.1087 Ag.

	Found.	Theory. $C_{18}H_{10}O_5Ag_2$.	$C_{18}H_{12}O_6Ag_2$.
C	40.66 per cent.	41.44	40.00 per cent.
H	2.32	1.91	2.22
Ag	40.52	41.29	40.00
O	16.50	15.35	17.77

This silver salt is very stable, being only slowly discolored on standing in the air by daylight. The solution of the ammonium salt gives the following reactions: Barium chloride precipitates the *barium salt* as a white amorphous mass, insoluble in water, but slightly soluble in alcohol. The *calcium salt* is thrown down by calcium chloride as a heavy, white, amorphous powder insoluble in water. Dried at 100° and analysed, it gave the following result:

0.2625 gram substance gave 0.0949 gram $CaSO_4$.

	Found.	Theory. $C_{18}H_{10}O_5Ca$.	$C_{18}H_{12}O_6Ca$.
Ca	10.63 per cent.	11.56 per cent.	10.99 per cent.

The *copper salt* is precipitated on the addition of cupric sulphate as a light-green, almost colorless mass, which is very sparingly soluble in water. It dissolves in ammonia and sodic hydroxide solution with a blue color.

On boiling these solutions, the salt is decomposed, copper oxide being precipitated.

Ferric chloride produces a reddish-brown precipitate, very much resembling that produced in solutions of benzoic acid or its salts.

Ferrous sulphate gives no precipitate.

On adding a solution of acetate of lead, the *lead salt* is thrown down as a heavy white mass, almost insoluble in water.

If a solution of zinc sulphate be added to the ammonia salt, the whole remains clear for some time, but after standing the *zinc salt* slowly separates out as a white powder, which is somewhat soluble in hot water.

The *nickel salt* is formed on adding a solution of sulphate of

nickel as a light-green precipitate, which is soluble in ammonia, producing a beautiful blue solution.

Action of Acetic Anhydride on the Acid $C_{18}H_{12}O_5$.

In order to obtain some clue as to the constitution of this acid, several experiments were tried with different reagents, mostly without result. On heating it with acetic anhydride, however, it was found that the acid easily gave up the elements of water, being converted into an indifferent body, according to the equation—

$$C_{18}H_{12}O_5 = C_{18}H_{10}O_4 + H_2O.$$

In order to examine this new compound, the pure acid, $C_{18}H_{12}O_5$, was heated with an excess of acetic anhydride for about an hour in a flask connected with a reflux condenser. On cooling, the solution which had become slightly yellowish was diluted with water and allowed to remain until the excess of acetic anhydride had dissolved. During this operation a beautifully crystalline substance separated, which was collected, well washed with water, recrystallised once from acetic acid, and analysed, with the following result:

0.1961 gram substance gave 0.0670 gram H_2O and 0.5329 gram CO_2.

	Found.	Calculated, $C_{18}H_{10}O_4$.
C	74.11 per cent.	74.48 per cent.
H	3.79	3.45
O	22.10	22.07

It melts at 254–255° with slight decomposition. If heated carefully in a test-tube, the greater part sublimes, but considerable decomposition takes place, and a black residue is left. The sublimate is crystalline, and probably identical with that obtained by treating the acid $C_{18}H_{12}O_5$ in the same way. The compound $C_{18}H_{10}O_4$ is sparingly soluble in hot alcohol, yielding a solution with a most beautiful violet fluorescence very much like that exhibited by anthracene. It is nearly insoluble in cold alcohol. The solution in hot alcohol gives an orange coloration with ferric chloride. The substance crystallises beautifully from its solution in hot glacial acetic acid, which on cooling deposits it in glittering plates. It is easily soluble in hot benzene, and on adding light petroleum is precipitated in a beautifully crystalline condition. It

is easily soluble in chloroform, but only sparingly in ether or bisulphide of carbon. It dissolves in concentrated sulphuric acid, yielding a yellowish-green solution which changes to a violet color on warming.

The compound $C_{18}H_{10}O_4$ is neutral, being almost insoluble in ammonia and potash solution, and apparently quite insoluble in sodic carbonate solution.

Action of Potash on the Compound $C_{18}H_{10}O_4$.

If this substance is warmed with fairly concentrated alcoholic potash, it dissolves without becoming discolored or any apparent decomposition taking place. In order to further examine this reaction, the liquid was heated for ten minutes on a water-bath, and then diluted with water, when the whole dissolved, forming a slightly yellowish solution. On adding dilute sulphuric acid, a solid acid was precipitated, which was collected, well washed with water, dissolved in alcohol, and filtered; in this way a small quantity of unchanged $C_{18}H_{10}O_4$ was easily removed. On evaporation, the filtrate deposited a solid crystalline acid, which after recrystallising from dilute acetic acid was analysed with the following result:

0.1865 gram substance gave 0.0668 gram H_2O and 0.4758 gram CO_2.

	Found.	Calculated, $C_{18}H_{12}O_5$.
C	69.58 per cent.	70.13 per cent.
H	3.98	3.89
O	26.44	25.97

This substance was, therefore, the original acid, $C_{18}H_{12}O_5$, formed from the compound $C_{18}H_{10}O_4$ by the addition of water, according to the equation,

$$C_{18}H_{12}O_4 + H_2O = C_{18}H_{12}O_5.$$

It melted at 230–235°, and had all the properties of the acid obtained by the action of dilute sulphuric acid on ethylic dibenzoylsuccinate.

Constitution of the Acid $C_{18}H_{10}O_5$.

Harrow by the action of dilute sulphuric acid on ethylic diacetylsuccinate[1] obtained carbopyrotritaric acid, $C_8H_8O_5$, which from his

analyses of its salts would seem to be a monobasic acid. When boiled with potash, however, it is converted into the potash salt of a bibasic acid, $C_8H_{10}O_6$, which gives salts of the formula $C_8H_5O_6M_2$.

The acid $C_{18}H_{12}O_5$ is, however, either bibasic or else very easily converted into a bibasic acid, as it gives directly salts containing two atoms of the metal; unfortunately, from the analyses it is not clear whether these have the formula $C_{18}H_{10}O_5M_2$ or $C_{18}H_{12}O_6M_2$. It is, however, possible that these acids, $C_{18}H_{12}O_5$ and $C_8H_8O_5$, are in reality anhydro-acids, the former acid when dissolved in ammonia or alkalis being converted into salts of an unstable acid, $C_{18}H_{14}O_6$.

Since the publication of an abstract of this research[1] the carbopyrotritaric acid has been more thoroughly examined by Knorr,[2] who considers it to be a bibasic acid forming salts of the formula $C_8H_6O_5Ag_2$. On account of the formation of ethylic carbopyrotritarate by the action of concentrated sulphuric acid on ethylic diacetylsuccinate in the cold, according to the equation,

$$C_{12}H_{18}O_6 - H_2O = C_{12}H_{16}O_5,$$

Knorr comes to the conclusion that carbopyrotritaric acid must have the following constitution:

$$\begin{array}{c} \text{COOH.C} : \text{C(CH}_3) \\ | \\ \text{COOH.C} : \text{C(CH}_3) \end{array}\!\!\!>\!\text{O},$$
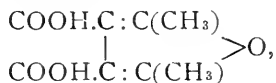
it being, in fact, dimethylfurfuranedicarboxylic acid. Since the publication of Knorr's research I have tried the action of concentrated sulphuric acid on ethylic dibenzoylsuccinate, and found that it behaves in exactly the same way as the diacetylsuccinate, although, unfortunately, having very little material at my command, I have not been able to analyse the immediate product corresponding with the ethylic carbopyrotritarate.

Ethylic dibenzoylsuccinate dissolves easily in concentrated sulphuric acid, the mixture becoming slightly warm and brownish colored. If water be added to it after standing for 15 hours, an oil is precipitated which soon becomes solid. This was extracted with ether, and on allowing the solution to evaporate, a beautiful substance was obtained, crystallising in long thick prisms melting at 85°. This is undoubtedly the diethyl salt of the acid $C_{18}H_{12}O_5$,

[1] Ber. **17**, 59.   [2] *Ibid.* **17**, 2863.

as on saponification with potash it gives the acid in a perfectly pure state, melting at 236–237°. In order to explain the formation of this acid, $C_{18}H_{12}O_5$, it is necessary in the first place to suppose the formula of ethylic dibenzoylsuccinate transformed into an isomeric unstable modification, thus :

$$\begin{matrix} COO(C_2H_5).CH.CO.C_6H_5 \\ | \\ COO(C_2H_5).CH.CO.C_6H_5 \end{matrix} = \begin{matrix} COO(C_2H_5).C : C(OH).C_6H_5 \\ | \\ COO(C_2H_5).C : C(OH).C_6H_5 \end{matrix}.$$
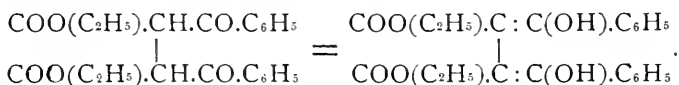
On treating this with sulphuric acid, water is eliminated, the diethyl salt of diphenylfurfuranedicarboxylic acid being formed, which therefore has the following constitution :

$$\begin{matrix} COO(C_2H_5).C : C(C_6H_5) \\ | \\ COO(C_2H_5).C : C(C_6H_5) \end{matrix} >O.$$
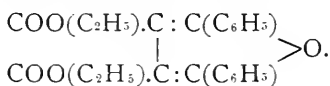
On saponification, this salt gives the acid $C_{18}H_{12}O_5$, thus :

$$C_{22}H_{20}O_5 + 2H_2O = C_{18}H_{12}O_5 + 2C_2H_5.OH.$$

The acid $C_{18}H_{12}O_5$ is therefore, without doubt, in reality diphenyl-furfuranedicarboxylic acid.

The compound $C_{18}H_{10}O_4$, produced by the action of acetic anhydride on diphenylfurfuranedicarboxylic acid, is probably the anhydride of the acid, it being reconverted into the same by the action of alkalis. Its constitution would, therefore, be represented by the formula,

$$O < \begin{matrix} CO.C : C(C_6H_5) \\ | \\ CO.C : C(C_6H_5) \end{matrix} >O.$$
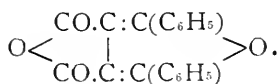
A further examination of these compounds is, however, necessary before these points can be settled.

In the paper published in the *Berichte* (*loc. cit.*), the splitting off of the water was supposed to take place between the carboxyl-groups and the hydroxyl-groups in the compound $\begin{matrix} COOH.C : C(OH)Ph \\ | \\ COOH.C : C(OH)Ph \end{matrix}$, the acid $C_{18}H_{12}O_5$ being a mono(γ)lactone and the compound $C_{18}H_{10}O_4$ a di(γ)lactone of dibenzoylsuccinic acid, and therefore having the formulae—
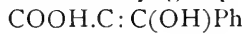
$$COOH.C < \begin{matrix} CH(CO.C_6H_5 \\ \\ C(C_6H_5) — O \end{matrix} >CO \quad \text{and} \quad O < \begin{matrix} C(C_6H_5) : C —— CO \\ | \\ CO —— C : C(C_6H_5) \end{matrix} >O.$$

Mono(γ)lactone.   Di(γ)lactone.
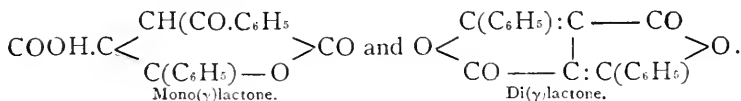
From Knorr's experiments, however, it would seem that his explanation of the formation of these bodies is the most probable, and that they are furfurane-derivatives, and not lactones.

Ethylic Monobenzoylsuccinate.

The examination of this substance was undertaken in the hope of throwing further light on the constitution of the compounds mentioned in the preceding section. If the acid $C_{18}H_{12}O_5$ is the γ-lactone of dibenzoylsuccinic acid, it was thought probable that the corresponding γ-lactone of monobenzoylsuccinic acid might be obtained by the action of dilute sulphuric acid on ethylic monobenzoylsuccinate, thus :

$$CO(C_6H_5).CH{<}^{COOH}_{CH_2.COOH} \qquad C(OH)(C_6H_5):C{<}^{COOH}_{CH_2.COOH}$$

<div align="center">Benzoylsuccinic acid.   Do. unstable form.</div>

$$COOH.C{<}^{C(C_6H_5)}_{CH_2.CO}{>}O .$$

<div align="center">γ-Lactone of benzoylsuccinic acid.</div>
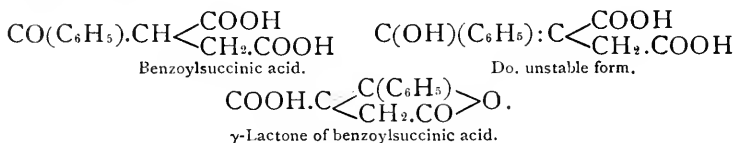
Ethylic benzoylsuccinate is easily obtained by treating the sodium compound of ethylic benzoylacetate with ethylic monochloracetate,

$$CO(C_6H_5).CHNa.COO(C_6H_5) + CH_2Cl.COO.C_2H_5 =$$
$$CO(C_6H_5).CH(COO.C_2H_5).CH_2.COO.C_2H_5 + NaCl.$$
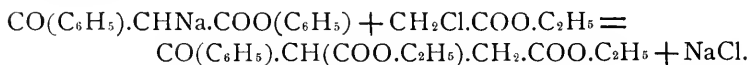
It was prepared as follows : 2.5 grams of sodium were dissolved in 30 grams of absolute alcohol, and then after well cooling, 20 grams of ethylic benzoylacetate and 12 grams of ethylic monochloracetate slowly added. The reaction takes place very slowly in the cold, but rapidly on a water-bath, the mixture after heating for two hours becoming perfectly neutral. In order to isolate the product, the alcohol was distilled off, and the residue then dissolved in water ; by this means a heavy oil separated out, which was extracted with ether. After drying over calcium chloride and distilling off the ether, a thick brownish oil was obtained, which unfortunately could not be made to crystallise.

On trying to distil this in a vacuum, it was found that only a small quantity went over undecomposed, the principal part frothing up and charring, a quantity of gas being at the same time given off. It is, however, comparatively easy to distil small quantities of about 5 grams, if the distillation is rapidly conducted. The distillates from several such operations were united and fractioned

once or twice, when an oil was obtained boiling at 260-265° (160 mm.); this gave the following numbers on analysis, agreeing with the formula of ethylic benzoylsuccinate:

0.1557 gram substance gave 0.0905 gram OH_2 and 0.3695 CO_2.

	Found.	Theory.
C	64.72 per cent.	64.75 per cent.
H	6.46	6.47
O	28.82	28.78

As thus obtained, it is a thick, almost colorless oil, of an agreeable aromatic smell, somewhat resembling that of ethylic benzoate. It boils at 260–265° (at 160 mm.). The pure compound is very stable, and may be distilled at the ordinary pressure, apparently without much decomposition. It is insoluble in water, but mixes with alcohol, ether, and the usual solvents. As on examination it was found that the crude product consisted of almost pure ethylic benzoylsuccinate, and as the distillation entailed great loss of valuable material, the crude compound was used in the following reactions and decompositions, after the excess of ethylic benzoyl-acetate had been removed by shaking the ethereal solution several times with dilute potash solution.

On the addition of a drop of ferric chloride to the solution of ethylic benzoylsuccinate in alcohol a beautiful claret color is produced. If heated for some hours on an oil-bath at about 250°, ethylic benzoylsuccinate is decomposed, lower boiling aromatic oils being formed, which, however, could not be further examined, on account of the smallness of the quantity obtained. It dissolves in concentrated sulphuric acid, producing a yellow solution, which becomes intensely red when heated.

It is decomposed by heating with alcoholic potash, a violet solution being produced, which on acidifying deposits a solid acid melting at 118–120°, probably benzoic or benzoylpropionic acid.

Like ethylic dibenzoylsuccinate, ethylic monobenzoylsuccinate gives a sodium compound when treated with sodium ethoxide.

This compound is easily prepared in the following way; 0.3 gram of sodium is dissolved in a small quantity of absolute alcohol, and then pure dry ether added until the whole has nearly dissolved. A solution of 3.5 grams of ethylic benzoylsuccinate in ether is then poured in, and the whole allowed to remain for some time. The mixture becomes violet-colored, and a gelatinous precipitate slowly

separates, which is collected and washed, first with a mixture of ether and alcohol, and lastly with pure ether. Dried over sulphuric acid in a vacuum, it gave the following numbers :

0.2601 gram substance gave 0.0680 gram Na_2So_4.

	Found.	Theory, $C_{15}H_{17}NaO_5$.
Na	8.47 per cent.	7.67 per cent.

It is a hard, almost colorless, apparently amorphous mass, which is moderately soluble in alcohol. If cupric acetate is added to this solution, the copper derivative is precipitated as a pale green amorphous mass, almost insoluble in water, but soluble in sodic hydroxide, producing a blue solution. Nitrate of silver and acetate of lead give white precipitates with the alcoholic solution of the sodium derivative. The sodium compound is very stable, much more so than the disodium derivative of ethylic dibenzoylsuccinate. The powdered substance is easily decomposed by treatment with acids, a yellowish oil being precipitated, probably regenerated ethylic monobenzoylsuccinate.

Decomposition Products of Ethylic Benzoylsuccinate.

Hydrolysis with Baryta-water.—Before examining the products of the hydrolysis with dilute sulphuric acid, it appeared to be interesting to study the action of alkalis, and for this purpose experiments were made with potash, but as this did not appear to give promising results, baryta-water was afterwards substituted for it, the method employed being the following :

Ethylic benzoylsuccinate was heated in a flask with an excess of a concentrated solution of barium hydroxide, by which means hydrolysis rapidly set in, the reaction being complete in about an hour. During the operation the oil disappeared, without the liquid becoming much discolored, and a heavy sandy precipitate of a brownish color slowly separated. This was collected, washed with water, and decomposed with hydrochloric acid, when traces of carbonic anhydride were given off. After extracting several times with ether, a dark-brown oil was obtained, which began to deposit crystals after some time. These were separated from the oily mother-liquor by extracting with chloroform, and thus obtained in a perfectly colorless state, melting at 180°, and having all the properties of succinic acid. In order to confirm this, the silver salt was prepared and analysed with the following result :

0.2024 gram substance gave 0.1306 gram silver.

	Found.	Theory, $C_4H_4O_4Ag_2$.
Ag	64.52 per cent.	65.07 per cent.

On acidifying with hydrochloric acid the filtrate from the precipitated baric succinate, it gave a quantity of a beautifully crystalline acid, which was collected, well washed, and recrystallised once or twice from water. It was thus obtained in silky needles melting at 118–120°, and was therefore either benzoic or benzoylpropionic acid. A silver salt was made and analysed with the following result:

0.1976 gram substance gave 0.0936 gram silver.

	Found.	Theory, C_6H_5COOAg.	Theory, $C_6H_5.CO.CH_2.CH_2.COOAg$.
Ag	47.37 per cent.	47.16 per cent.	37.82 per cent.

The acid was evidently benzoic acid.

Ethylic benzoylsuccinate is therefore decomposed by boiling with concentrated baryta-water into benzoic and succinic acids, thus:

$$C_6H_5.CO.CH(COO.C_2H_5).CH_2.COO.C_2H_5 + 3H_2O =$$
$$C_6H_5.COOH + C_2H_4(COOH)_2 + 2C_2H_5.OH.$$
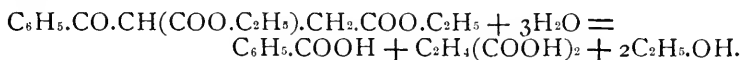
In this respect it differs somewhat from ethylic acetylsuccinate, which on hydrolysis with dilute baryta-water, is split up into acetylpropionic acid and carbonic anhydride, only a small quantity of acetic acid and succinic acid being formed.[1]

Ethylic benzoylsuccinate, if treated with dilute baryta-water, might also be split up in this way into benzoylpropionic acid and carbonic anhydride.

Hydrolysis with Dilute Sulphuric Acid.—Ethylic benzoylsuccinate was heated with a large excess of dilute sulphuric acid (1 : 2) in a flask connected with a reflux condenser, at the end of which a test-tube containing baryta-water was attached. The oil became more and more darkly colored, and large quantities of carbonic anhydride were given off, until at the end of about fifteen hours most of the ethereal salt had dissolved, a small quantity of a tarry substance being left. On cooling, the liquid became filled with glittering crystals, which were collected, well washed with water, roughly separated from oily mother-liquor by spreading

[1] Conrad, Annalen **118,** 218.

out on a porous plate, and then recrystallised once or twice from water, animal charcoal being used to decolorise the liquid. In this way, the body was obtained in glittering plates melting at 117°, and closely resembling benzoic acid. The analysis, however, showed the body to be benzoylpropionic acid.

0.2230 gram substance gave 0.1132 gram OH_2 and 0.5487 gram CO_2.

	Found.	Theory, $C_{10}H_{10}O_3$.
C	67.12 per cent.	67.41 per cent.
H	5.64	5.62
O	27.24	26.97

Ethylic benzoylsuccinate splits up, therefore, on boiling with dilute sulphuric acid into benzoylpropionic acid and carbonic anhydride according to the equation—

$$CO(C_6H_5).CH(COO.C_2H_5).CH_2.COO.C_2H_5 + 2H_2O =$$
$$CO.C_2H_5.CH_2.CH_2.COOH + CO_2 + 2C_2H_5.OH.$$
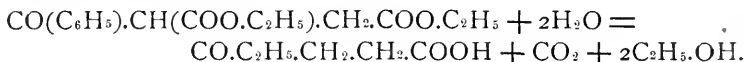
Benzoylpropionic acid has already been obtained (1) by the action of aluminic chloride on a mixture of succinic anhydride and benzene,[1] and by the reduction of benzoylacrylic acid.[2] The acid obtained from ethylic benzoylsuccinate agrees with that produced by the above two reactions in every respect.

By modifying the conditions in the hydrolysis of *ethylic benzoyl-succinate* with dilute sulphuric acid, the same results were always obtained, no lactone ever being formed. The reason for this is that the C_2H_5 group of the $COO.C_2H_5$, which is joined to the $C_6H_5.CO.CH$, in benzoylsuccinic ether, is always split off first, forming the unstable acid $C_6H_5.CO.CH(COOH).CH_2.COO.C_2H_5$, which then naturally loses carbonic anhydride, and is converted into ethylic benzoylpropionate, this being then further hydrolysed by the action of the sulphuric acid. Analogous results were obtained by Conrad[3] by the action of dilute sulphuric acid on ethylic acetylsuccinate, acetylpropionic acid, ethylic acetylpro-pionate and carbonic anhydride being the products of the reaction.

[1] Burcker, Bull. Soc. Chim. **35**, 17.   [2] Pechmann, Ber. **14**, 889.   [3] Ber. **11**, 2177.

[*To be continued.*]

ON THE DETERMINATION OF ARSENIC.

By LeRoy W. McCay.

Arsenic and its compounds have until lately proved very unsatisfactory things for the chemist to determine. There are indeed few common elements the quantitative estimation of which has, up to within the last few years, presented such numerous, persistent and extraordinary difficulties as the one forming the subject of this paper. As a matter of fact there is, at the present day, no gravimetric method for estimating arsenic which is not without fault. The one most commonly used, that of Levol, is, open to at least two serious objections. In the first place, the ammonium magnesium arseniate is perceptibly soluble in ammonia water, and in the second place, the danger of occasioning a loss of arsenic by the reducing action of the ammonia upon igniting the salt is a fact too well known to need mention. Chemists, it will be remembered, have endeavored to avoid the error arising in the first instance by the addition of alcohol to the solution to be precipitated, but even in ammoniacal alcohol the double arseniate is sensibly soluble; consequently, although considerably reduced, the error cannot be said to be entirely eliminated. Attempts have also been made, and that too with a considerable amount of success, to avoid the error arising in the second instance by removing the salt particles adhering to the filter paper with dilute nitric acid, moistening the precipitate with the same reagent, and igniting—at first gently, then strongly. Much skill and care, however, is requisite in the process of igniting; it being no uncommon occurrence, when the heat is too suddenly applied, to drive off a portion of the ammonia at such a rate as to occasion considerable reduction, even in such a strong oxidising atmosphere as nitrous oxide.[1]

Not long since Bunsen[2] published an article upon the separation of arsenic and antimony and upon the determination of each as sulphide. The separation of the two elements is quick, easy and

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[1] Brauner, who proposes the igniting of the precipitate in an atmosphere of nitrous oxide, directs that the salt be brought into a small thin porcelain crucible, that this crucible be placed in a larger one of platinum, and that the heat be then applied, very gently at first, then gradually stronger, until the full capacity of the burner is reached.

[2] Zeitschr. f. analy. Chem. **16**, 57. See also Reichel, Zeitschr. f. analy. Chem. **20**, 89.

accurate. As regards the estimation of the arsenic, however, it is, as Fresenius has already intimated, undoubtedly necessary, in order to ensure correct results, to follow Bunsen's details to the letter; for although the sulphide obtained by precipitating the arsenic from a solution thoroughly treated with chlorine has, after having undergone a detailed course of washing, exactly the composition of arsenic pentasulphide, and is in fact regarded by Bunsen as being such, it must not be forgotten that no less an authority than Rose[1] declares the precipitate occasioned by sulphuretted hydrogen in solutions of arsenic acid to be not pure arsenic pentasulphide, As_2S_5, but a mixture of the trisulphide, As_2S_3, and sulphur. If Rose's statement is true, then the chances are that a slight departure from the directions as given by Bunsen might occasion incorrect results in the determination of the element. Besides the objection to be found in the uncertainty as to the actual character of the sulphide obtained by neglecting to follow Bunsen's details absolutely, another and serious one can be urged against the necessity of being compelled to weigh the precipitate on a tared filter paper after having thoroughly dried at $110°$ C. I willingly grant that the Bunsen method furnishes perfectly correct results, and that it is a wonderful improvement upon the old method of Levol; still it is a long, tedious and unpleasant operation. The arsenic is precipitated very slowly from the solution of arsenic acid, and unless the precipitate is filtered off at just the right point some arsenic is sure to remain in solution. The precipitation, in fact, requires much attention, patience and practice, and in consequence thereof it is with much pleasure and satisfaction that we welcome the beautiful proposal of Carl Holthof.[2]

Mohr's method for estimating arsenic is one of the most simple and exact in the field of analytical chemistry. It presupposes, however, the existence of the arsenic in the state of arsenious acid, a condition which is rarely fulfilled inasmuch as in the regular course of analysis arsenic is almost invariably obtained as arsenic trisulphide or arsenic acid. The method, it will be remembered, depends upon the fact that in a weakly alkaline solution arsenic in

[1] Rose, Pog. Ann. **107**, 186. Wackenroder arrived at the same results prior to Rose. See Ludwig's investigations, Ar. d. Pharm. 2 Reihe, **97**, 32. Also A. Fuchs, Zeitschr. f. analy. Chem. **81**, 189.

[2] Holthof, Zeitschr. f. analy. Chem. **23**, 378.

the state of arsenious acid is oxidised by iodine to arsenic acid, in accordance with the equation :

$$H_3AsO_3 + 2I + H_2O = H_3AsO_4 + 2HI.$$
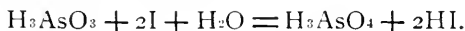
The difficulty of obtaining the arsenic in the minimum state of oxidation has caused the method of Mohr to fall into neglect and consequently escape that attention which is due it.

Many years ago Holthof obtained very satisfactory results by carefully oxidising small quantities of sulphide of arsenic with nitric acid in a porcelain dish, evaporating to dryness with a few drops of sulphuric acid, and boiling down in a large beaker to one-third the original volume, after having first added one-third of a litre of sulphurous acid solution, then refilling to the mark with sulphurous acid solution, and again evaporating to one-third the original volume, neutralising, after cooling, with sodium carbonate, adding a constant quantity of mono-sodium carbonate, a little starch solution, and titrating with a standard solution of iodine. Holthof evidently did not at that time publish anything relating to this method of determining arsenic, for in speaking of it in the first part of his recent paper he makes no reference to any work or periodical. A little over a year ago, at the instigation and in the laboratory of Fresenius in Wiesbaden, he undertook a thorough study of the process, it being his chief object to discover whether the mode of procedure was applicable in the case of large quantities of arsenic, and also practicable in determining the arsenic in the strong hydrochloric acid solution which is obtained when working according to the Bunsen separation method. It will be at once evident that the success of the method depends upon the complete reduction of the arsenic from the arsenic to the arsenious state of oxidation. Holthof starts out with the assumption [1] that when a sufficient quantity of sulphurous acid is used, and the solution is heated for a sufficient length of time, the reduction is complete, and in the end he proves that this is the case.

In brief Holthof's method is as follows : 1. The solution containing about 0.10–0.20 gram arsenious oxide, As_2O_3, as arsenic oxide, As_2O_5, is brought to 50 cc. and diluted in a flask with 100–150 cc. sulphurous acid and 150–200 cc. water. The flask with its contents is then heated for four hours, and next boiled down over a free flame to one-half the original volume. A little clear starch

[1] See the communication of Wöhler, Ann. d. Chem. und Pharm. **30**, 224.

solution is now run in, 40 cc. of a solution of hydro-sodium carbonate saturated in the cold added, the whole diluted to about one-third of a litre and titrated to a light sky-blue, with a standard solution of iodine containing approximately 10.0 grams iodine to the litre. The test analyses, although not numerous, are very satisfactory.

2. Holthof did not experiment upon sulphide of arsenic, at all events not in the case before us, but his thorough study of the oxidising action of chlorine upon the arsenious acid, and his examination of the question relating to the volatility of arsenic trichloride when a solution of arsenic acid is evaporated to dryness with excess of hydrochloric acid, justify us in presuming that, according to him, the following would be the method of procedure in the case of sulphide of arsenic.[1] The sulphide of arsenic is brought into a little porcelain dish provided with a watch-glass cover, and treated either with fuming nitric acid or potassium chlorate and hydrochloric acid until solution is complete. The liquid is then evaporated, a few drops of sulphuric acid added, diluted, reduced as already described, boiled down to one-half the original volume, cooled, evaporated to about 300 cc., and titrated to a light blue. The test analyses resulting from evaporating arsenic pentoxide, As_2O_5, solutions in the presence of excess of chlorine and hydrochloric acid are good, and prove conclusively that when arsenic acid, chlorine and hydrochloric acid are evaporated upon the water-bath no arsenic is volatilised as trichloride. The two sets of experiments then prove :

1st. That the reduction with sulphurous acid is complete; 2d. that upon evaporating arsenic pentoxide, As_2O_5, in the presence of hydrochloric acid, no arsenic escapes as trichloride.

Holthof concludes from the above that not only is the method suitable for technical needs, but also that its exactness renders it worthy of being used for scientific purposes.

For some time past I have been engaged in making a thorough examination of the method of Holthof, and I have reached the conclusion that it is the most perfect one at present known. Further, by taking advantage of a device of my own, the time requisite for making a determination is reduced to a minimum. At the outset I went over Holthof's work for the purpose of

[1] See his method of procedure as practised in former years.

determining whether the reduction, when made in strict accordance with his directions, is so complete as to render it impossible to detect, by qualitative measure, any arsenic acid in the liquid after boiling down to one-half the original volume and then carefully evaporating to about 50 cc.

In order to obtain a solution suitable for qualitative as well as quantitative experiments, I dissolved 28.90 grams H_2KAsO_4 in about 250 cc. water and diluted to two litres. Theoretically every 10 cc. of this solution should contain 0.0602 gram $As =$ 0.0794 gram $As_2O_3 = 0.0923$ gram As_2O_5. However, being ignorant as to the exact degree of purity of the salt, the solution was carefully analysed: 1st. by the method of Levol; 2d. by the method of Reich.

1st. 10 cc. were put into a small beaker, rendered strongly acid with hydrochloric acid, then strongly alkaline with ammonia, cooled, and finally precipitated with magnesia mixture, care being taken to add this reagent slowly, drop by drop, and with constant stirring. After standing twelve hours the ammonium magnesium arseniate was filtered off, washed with ammoniacal water, dried, moistened with nitric acid and ignited—all details relating to the extraction of the particles of the salt from the filter paper with dilute nitric acid being strictly observed. The 10 cc. gave 0.1215 gram $Mg_2As_2O_7 = 0.0591$ gram $As = 0.0780$ gram $As_2O_3 = 0.0906$ gram As_2O_5. These figures, it will be observed, are somewhat lower than those required by theory.

2d. *Three Estimations.*—*a.* One volumetrically; *b.* two gravimetrically.

a. 10 cc. were put into a small beaker, about 50 cc. water added, and enough ammonia to produce a decided alkaline reaction dropped in. The solution was then heated to boiling, and a quantity of silver nitrate sufficient to ensure complete precipitation of the arsenic run in. The liquid was now stirred briskly until the precipitate exhibited a tendency to settle, leaving the supernatant fluid clear. The beaker with its contents was next removed from the flame, and ammonia water added to faint but distinct alkaline reaction. This alkaline reaction was removed by the aid of a drop of acetic acid, the liquid again thoroughly stirred, the whole allowed to stand for a few minutes, and, after entire subsidence, the silver arseniate filtered off, washed with pure cold water, dissolved off the filter paper with a little dilute nitric acid,

and the combined silver determined according to Volhard.[1] I found 0.2572 gram $Ag = 0.0595$ gram $As = 0.0785$ gram $As_2O_3 = 0.0912$ gram As_2O_5. The method of neutralising the solution is my own.

b. For the two estimations made gravimetrically and according to my own modification[2] of the Reich process, I used in each case 10 cc. The precipitation of the arsenic was made exactly as above described, but instead of dissolving the silver arseniate in nitric acid and titrating the silver, the precipitate was removed from the filter paper by means of a few drops of ammonia and a little water, the solution caught in a small weighed platinum dish, evaporated to dryness, the residue heated for a short time at 100° C. and then weighed. From the formula Ag_3AsO_4 the arsenic was calculated. I found (1) 0.3661 gram $Ag_3AsO_4 = 0.0592$ gram $As = 0.0781$ gram $As_2O_3 = 0.0907$ gram As_2O_5; (2) 0.3659 gram $Ag_3AsO_4 = 0.0592$ gram $As = 0.0781$ gram $As_2O_3 = 0.0907$ gram As_2O_5. Since the molecular weight of $Ag_3AsO_4 = 463$, and the atomic weight of $As = 75$, the relation between the two is about $6:1$, or a difference of six milligrams in the weight of the silver salt will occasion a difference of but one milligram in the weight of the arsenic. The wonderful degree of accuracy of the method is at once evident. The Levol method gave 0.0591 gram metallic arsenic ; the Reich method 0.0593 gram of the element in 10 cc. The difference, 0.0002 gram, is due probably to the solubility of the ammonium magnesium arseniate in ammoniacal water. The figure 0.0593 is undoubtedly the correct one, and we shall in our future work regard it as such.

The following are the *qualitative* tests made according to Holthof's directions, my object here being, as already intimated, to satisfy myself as to the exact degree of completeness of the reduction of the arsenic from the arsenic to the arsenious state of oxidation. In I, each of the 10 cc. of H_2KAsO_4 solution taken were mixed in a flask with 50 cc. sulphurous acid and 100 cc. water, after which the flask and contents were heated for two hours upon the boiling water-bath, then for two hours to incipient boiling upon a little sand-bath, whereupon the liquid was boiled down over a free flame to one-half the original volume ; a large platinum

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[1] Pearce's modification of the Reich method; For particulars see Engineering and Mining Journal **35**, 256. See also Chemical News **48**, 85.

[2] For another modification see Chemical News **48**, 7 and 168.

spiral with pieces of pumice about the size of hazel-nuts threaded and twisted on each end being introduced into the flask, partially to prevent bumping, partially to facilitate the disengagement of the sulphur-dioxide gas. In II, double the quantities of sulphurous acid and water used in I were added, and in III, first the quantities used in I, second those used in II. In each case the liquid remaining after boiling down was emptied into a porcelain dish, evaporated to about 50–60 cc. and tested for arsenic acid (1) with silver nitrate, (2) with magnesia mixture, and (3) with magnesia mixture after removing the arsenic as the trisulphide with sulphuretted hydrogen in the cold and displacing the latter with a rapid stream of carbon dioxide. The tests were made in strict accordance with the directions of Fresenius.[1] In no case was I able to obtain in the 50–60 cc. a decided reaction for arsenic acid. For sake of convenience I arrange the experiments in outline as follows :

I.

    a. 10 cc. solution, 50 cc. SO_2 and 100 cc. H_2O.
    b.   "   "   "   "

a. Reaction for As_2O_5 with $AgNO_3$, none. *b.* Reaction for As_2O_5 with magnesia mixture, none.

II.

    a. 20 cc. solution, 100 cc. SO_2 and 200 cc. H_2O.
    b.   "   "   "   "

a. Reaction for As_2O_5 with $AgNO_3$, none. *b.* Reaction for As_2O_5 with magnesia mixture, none.

III.

    a. 10 cc. solution, 50 cc. SO_2 and 100 cc. H_2O.
    b. 20 cc. solution, 100 cc. SO_2 and 200 cc. H_2O.

a. Reaction for As_2O_5 with magnesia mixture, after separation of As_2O_3, none. *b.* Reaction for As_2O_5 with magnesia mixture, after separation of As_2O_3, none.

These experiments go to prove that the reduction of the arsenic from the arsenic to arsenious state is to all intents and purposes complete, and in consequence thereof they confirm conclusively

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[1] Fresenius, Anleitung zur qualit. chem. Analyse, 14 Aufl. **199,** 9.

what Holthof has to say respecting the correctness of his mode of procedure. For quantitative work much experience has led me to believe that the following solutions are probably the most convenient:

(*a*) $\frac{1}{40}$ *Normal iodine solution.*[1]—Dissolve 6.35 grams of pure dry iodine with the help of about 10.0 grams of potassium iodide in a little water and dilute to a litre.

(*b*) $\frac{1}{40}$ *Normal arsenious oxide solution.*[1]—Dissolve 2.475 grams chemically pure arsenious oxide in a little warm potassium hydrate solution, neutralise with hydrochloric acid and dilute to a litre.

Use for controlling the iodine solution:

(*c*) *Starch solution.*[2]—Rub up thoroughly in a small porcelain mortar, with 10 cc. of a solution of pure potassium hydrate of ordinary strength, two grams of starch and bring into 200 cc. boiling water. Stir until solution is complete, cool bottle and preserve well corked. It will keep indefinitely.

(*d*) *Hydro-sodium carbonate.*—Dissolve 150–200 grams of the pure salt in two litres of water.

(*e*) *Sulphurous acid.*—Use water *saturated*[3] with the gas.

Theoretically, 1 cc. of the above $\frac{1}{40}$ normal iodine should exactly balance 1 cc. of the $\frac{1}{40}$ normal arsenious oxide, and 1 cc. $= 0.001875$ gram $As = 0.002475$ gram $As_2O_3 = 0.002875$ gram As_2O_5; practically, however, 20 cc. of the arsenious oxide solution required, in three separate trials, (1) 19.9, (2) 19.9, and (3) 19.9 cc. of the iodine solution for complete oxidation. Hence 1 cc. $= 0.001884$ gram $As = 0.002487$ gram $As_2O_3 = 0.002889$ gram As_2O_5.

A. 1.—50 cc. of the solution H_2KAsO_4, 100 cc. SO_2 and 150 cc. water were brought into a flask and heated for two hours upon a boiling water-bath, then for two hours upon a little sand-bath, and finally boiled down to one-half the original volume, a large platinum spiral being introduced into the flask to prevent bumping and facilitate the disengagement of the sulphur-dioxide gas. In all my experiments this boiling down to one-half the original volume (care being of course taken to introduce into the flask the platinum spiral) proved amply sufficient. I have not yet been able to detect any sulphur dioxide in a solution so treated.

[1] Modern system. See Clemens Winkler's Maassanalyse, Freiberg, 1883.
[2] Alex. Müller, Landw. Versuchs-Stationen **27**, 340. See also Zeitschr. f. analy. Chem. **22**, 76.
[3] This solution should be as strong as possible.

The solution was allowed to cool, diluted to 300 cc., and for each of the first lot of estimations below given 30 cc., for each of the second lot 60 cc. taken. In tritrating care was taken always to work under like conditions—the same quantities of hydro-sodium carbonate, starch and water being invariably used. The most convenient volume of liquid for titration proved to be approximately 300 cc. Accordingly, 30 cc. reduced solution, 20 cc. hydro-sodium carbonate and 1 cc. starch solution being diluted in a larger beaker to 300 cc., the $\frac{1}{40}$ normal iodine solution was run in until a sky-blue color resulted. The point of transition is remarkably easy to strike, and the reaction is so sharp and exact that one is never in doubt as to a single drop. The fact too that the blue appears shortly before the oxidation is complete and a little extra stirring is necessary to cause it to disappear, furnishes us with an indication of the approach of the end of the operation, and thereby renders it almost impossible for one to overstep the point.

Four estimations :

No.	Red. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	30 cc.	15.7 cc.	0.0295 gram.	0.0390 gram.	0.0453 gram.
2	30	15.7	0.0295	0.0390	0.0453
3	30	15.7	0.0295	0.0390	0.0453
4	30	15.75	0.0296	0.0391	0.0454

Actually present:

$$As = 0.0296 = 0.0390, As_2O_3 = 0.0453 \; As_2O_5.$$

Three estimations :

No.	Red. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	60 cc.	31.5 cc.	0.0593 gram.	0.0783 gram.	0.0910 gram.
2	60	31.5	0.0593	0.0783	0.0910
3	60	31.6	0.0595	0.0785	0.0915

Actually present :

$As = 0.0593$ gram $= 0.0782$ gram, $As_2O_3 = 0.0907$ gram As_2O_5.

2.—100 cc. H_2KAsO_4, 150 cc. SO_2 solution and 200 cc. water were brought into a flask and reduced as above described. After boiling the liquid down to one-half the original volume, cooling and diluting to 1000 cc., the following results were obtained. For each determination 100 cc. solution were taken.

No.	Red. Solution	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	100 cc.	31.7 cc.	0.0597 gram.	0.0788 gram.	0.0916 gram.
2	100	31.8	0.0599	0.0791	0.0918
3	100	31.7	0.0597	0.0788	0.0916
4	100	31.8	0.0599	0.0991	0.0918

50 cc. of same solution required 15.9 cc. $\frac{1}{40}$ normal iodine $=$ 0.02995 As $=$ 0.0395 As$_2$O$_3$ $=$ 0.0459 As$_2$O$_5$.

The average number of cc. of $\frac{1}{40}$ normal iodine used in this lot of tests is 31.75, the average number used in the lot immediately preceding is 31.53; the difference between the two is 0.22 cc. This 0.22 is a distinct plus, and requires explanation in spite of the fact that owing to the extremely dilute iodine solution it is too small to occasion any decidedly appreciable error in the results. The excess is, I am inclined to believe, probably due to the action on the iodine of organic matter in the distilled water, the destructive capacity of this matter as regards iodine increasing, as a matter of course, with the increase in the quantity of water used, as well as with the length of time requisite for reducing and boiling down to the required volume. It will be observed that in the second experiment more water was used than in the first, and in consequence thereof that the time necessary for reducing and boiling down is greater in the latter than in the former case.

B. 1.—To test the method further, I brought 2.475 grams As$_2$O$_4$ into a litre-flask with a long, narrow neck, added 100 cc. pure nitric acid, and, having clamped the flask in an inclined position in the water-bath, heated the contents to boiling. As soon as all reaction had ceased, the flask and contents were removed from the bath, and heated gently over a free flame until all hyponitric oxide fumes had disappeared and the solution was clear and colorless. 20 cc. dilute sulphuric acid were then added, the solution was transferred to a porcelain dish, evaporated down until every trace of nitric acid was expelled, cooled, neutralised, and diluted to a litre. 50 cc. of this solution were mixed with 150 cc. SO$_2$ solution, 200 cc. water added, and the whole was treated as already described —for two hours on the water-bath, two hours on the sand-bath, and finally boiled down over a free flame to a little less than one-half the original volume. The liquid after cooling was diluted to exactly 200 cc., and for each of the following tests 50 cc. taken.

No.	Red. Solution.	1-40 Normal Iodine.	As.	As$_2$O$_3$.	As$_2$O$_5$.
1	50 cc.	12.5 cc.	0.0235 gram.	0.0311 gram.	0.0361 gram.
2	50	12.5	0.0235	0.0311	0.0361
3	50	12.5	0.0235	0.0311	0.0361
4	50	12.5	0.0237	0.0313	0.0363

Since 1000 cc. standard solution $=$ 2.475 grams As$_2$O$_3$, 50 cc. $=$

0.12375 gram As_2O_3; and since the 50 cc. were after reduction and boiling down diluted to 200 cc., 50 cc. or $\frac{1}{4}$ of 200 cc. $= 0.0309$ gram As_2O_3, a figure which agrees very well with that found by analysis.

2. 100 cc. standard solution, 200 cc. SO_2 solution and 200 cc. water were reduced, boiled down, cooled and diluted to 500 cc. Four tests were made, each with 100 cc.

No.	Red. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	100 cc.	20.1 cc.	0.0378 gram	0.0499 gram	0.058 gram
2	100	20.1	0.0378	0.0499	0.058
3	100	20.05	0.0377	0.0498	0.058
4	100	20.1	0.0378	0.0499	0.058

Theory demands :

$$0.0375 \ As = 0.0495 \ As_2O_3 = 0.0575 \ As_2O_5.$$

20 cc. of the standard solution should require, after reduction, 19.9 cc. $\frac{1}{40}$ normal iodine, whereas, as will be seen, 20.1 cc. were used. The cause of the error, 0.22 cc., has already been suggested. The error is so small that it in no case materially affects the accuracy of the results.

Having had occasion during my examination of the Holthof method to subject several organic compounds at high temperatures and under pressure to the oxidising influence of certain reagents, the thought suggested itself that, perhaps, by acting on arsenic acid with sulphurous acid under pressure, the reduction of the former to the lower stage of oxidation might be easily accomplished, and that too in a comparatively short period of time. The results of some qualitative experiments in this direction will be found in the *Chemical News*, Vol. 51, No. 1320, March 13th, 1885. The results obtained were very satisfactory, and seemed to prove without a doubt that when arsenic acid, sulphurous acid and water are heated for one hour in hermetically closed flasks and at a temperature equal to that of boiling water, the arsenic acid is completely reduced to arsenious acid. In my article in the *Chemical News* I have given the results of seven experiments, the quantity of arsenic as arsenic acid in each test ranging from 0.06 to 0.90 gram. In every case excepting one the reduction was complete. In the last experiment (0.9 gram arsenic acid present) 20 cc. of the reduced solution gave with magnesia mixture, after

boiling off the sulphur dioxide, a slight reaction for arsenic acid —one so slight, however, that upon filtering off the precipitate and dissolving it in a drop of nitric acid, no reddish-brown color or precipitate was obtained with silver nitrate and ammonia. In all the seven experiments my tests were made upon *portions* of the reduced solution, consequently it seemed well before trying the process quantitatively, again to make a series of experiments, using the entire quantity of the reduced liquid for a test exactly as was done in my examination of the Holthof method of reduction.

I proceeded as follows.

The solution of H_2KAsO_4 was brought into a little bottle provided with a well-fitting ground-glass stopper, and capable of withstanding a pressure corresponding to the heat of a boiling water-bath, a strong solution of sulphurous acid run in, the bottle tightly stoppered and the stopper firmly tied down with a piece of cord. The bottle was next placed in a water-bath, the contents of which had been brought to active boiling, and here permitted to remain for exactly one hour. After cooling, the reduced liquid was emptied into a flask, diluted to about 150 cc. and boiled down to one-half the volume, care being taken to introduce into the flask a large platinum spiral. It was then transferred to a porcelain dish, evaporated to 50 cc., filtered, and tested for arsenic acid (1) with silver nitrate, and (2) with magnesia mixture.[1] Six tests were made, but in no case could I, after boiling down, obtain in the 50 cc. a definite reaction for arsenic acid.

I.

10 cc. H_2KAsO_4 solution ;
20 cc. SO_2 solution.

10 cc. $= 0.0593$ gram $As = 0.0782$ gram $As_2O_3 = 0.090$ gram As_2O_5.
Reaction for As_2O_5 with silver nitrate, none.

II.

10 cc. H_2KAsO_4 solution ;
20 cc. SO_2 solution.

10 cc. $= 0.0593$ gram $As = 0.0772$ gram $As_2O_3 = 0.090$ gram As_2O_5.
Reaction for As_2O_5 with magnesia mixture, none.

[1] The solutions stood 12—24 hours.

III.

20 cc. H_2KAsO_4 solution ;
30 cc. SO_2 solution.

20 cc. $=$ 0.1186 gram As $=$ 0.1564 gram $As_2O_3 =$ 0.180 gram As_2O_5.
Reaction for As_2O_5 with silver nitrate, none.

IV.

20 cc. H_2KAsO_4 solution ;
30 cc. SO_2 solution.

20 cc. $=$ 0.1186 gram As $=$ 0.1564 gram $As_2O_3 =$ 0.180 gram As_2O_5.
Reaction for As_2O_5 with magnesia mixture, none.

V.

30 cc. H_2KAsO_4 solution ;
40 cc. SO_2 solution.

30 cc. $=$ 0.1779 gram As $=$ 0.2346 gram $As_2O_3 =$ 0.270 gram As_2O_5.
Reaction for As_2O_5 with silver nitrate, none.

VI.

30 cc. H_2KAsO_4 solution ;
40 cc. SO_2 solution.

30 cc. $=$ 0.1779 gram As $=$ 0.2346 gram $As_2O_3 =$ 0.270 gram As_2O_5.
Reaction for As_2O_5 with magnesia mixture, none.

Having worked so satisfactorily qualitatively, I determined to see whether this method of reduction could not be made to take the place of that suggested by Holthof; it being plain that, should its practicability prove incontestable, the Mohr-Holthof process would be wonderfully improved, especially in respect to the time necessary for making a reduction. When working according to Holthof, considerable quantities of sulphurous acid and *four* hours are requisite for complete reduction ; whereas, by subjecting the arsenic acid under pressure to the reducing influence of the sulphurous acid, the reduction is accomplished in *one* hour. It is just here that I propose to modify the method.

Since the reduction of arsenic to arsenious acid with sulphurous acid is, when all the details above indicated are strictly observed,

not only complete, but also capable of being carried out in a remarkably short period of time, it seemed feasible to make a few estimations of the element as the sulphide; this method of determining the arsenic being especially applicable in the case of a solution containing pure arsenious acid, and free from all substances possessing the property of acting in a reducing manner upon sulphuretted hydrogen.

The determinations were made by bringing the solution of H_2KAsO_4 into a little bottle of convenient size, adding some-what over an equal volume of *strong* sulphurous acid and reducing, then boiling down one-half after transferring to a flask, and precipitating the arsenic in a beaker with freshly prepared sulphuretted hydrogen water. The solution when ready for pre-cipitation should be moderately hot, strongly acid, and its volume should equal about 100 cc. The freshly prepared and perfectly clear sulphuretted hydrogen water is to be added in slight excess, and the solution, after the addition of the same, heated on the sand-bath to about 80-85°, and kept at this temperature with occasional stirring until the precipitate of the sulphide settles com-pletely, leaving the supernatant fluid clear, and emitting but a faint odor of sulphuretted hydrogen. The filtrates, although invariably examined, gave no evidence of the presence of arsenic.

Friedrich Mohr, in his *Lehrbuch der Titrirmethode*, IV Auflage, S. 357, uses the following language : "When the arsenic as arsenic trisulphide is once gotten upon the filter paper, nothing is simpler than to dissolve the same off the paper in ammonic hydrate and evaporate the resulting solution to dryness in a watch-glass or porcelain dish. I have satisfied myself that *dry* arsenic trisulphide when weighed in a platinum dish, dissolved in ammonic hydrate and again evaporated to dryness, gives exactly the same weight. From 0.243 gram As_2S_3 I obtained 0.243 gram, from 0.643 gram I got back 0.642 gram. It is only the filter paper which hinders the weighing and drying, and this is here done away with." Neither Rose, Fresenius nor Classen recommends this method of treating the precipitate of the sulphide, and I therefore thought it well to put it to the test. I made six determinations, the ammoniacal solution being caught, evaporated and weighed in a thin, light platinum dish. The sulphide was not dried, but dis-solved off the paper as soon as the washing was finished. Mohr's experiments were made on the *dry* sulphide, although from his

directions one would conclude that he advocated too the direct application of the ammonia to the still moist precipitate. Whether or not correct results would be obtained by first drying and then dissolving the precipitate I am unable to say. The following are the results of my experiments :

No.	St. Sol.	As_2S_3.	As.	As_3O_3.	As_2O_5.
I	10 cc.	0.0965 gram.	0.0588 gram.	0.0776 gram.	0.0901 gram.
2	10	0.0955	0.0582	0.0768	0.0892
3	10	0.0963	0.0586	0.0774	0.0898
4	10	0 0945	0.0576	0.0759	0.0883
5	10	0.0985	0.0600	0.0792	0.0920
6	10	0.1003	0.0611	0.0806	0.0936

10 cc. $= 0.0593$ gram As $= 0.0782$ gram $As_2O_3 = 0.0907$ gram As_2O_5.

The above results are not only incorrect, but they exhibit no constancy among themselves, in spite of the fact that in all cases extreme care was taken to work under like conditions. During the evaporation of the ammoniacal solution, one of the first things which attracted any attention was an evolution of sulphuretted hydrogen which continued until the last traces of moisture had disappeared and the residue exhibited a perfectly dry appearance. The presence of the sulphuretted hydrogen could be distinctly indicated by the change of color to brown, and in some cases almost to black, of a piece of filter paper moistened with a little acetate of lead solution and held over the platinum dish containing the solution of arsenic. The figures above given show conclusively that Mohr's proposal is inapplicable, at all events in the case of freshly precipitated and still moist trisulphide of arsenic. Numbers 1, 2, 3 and 4 are too low ; number 5 is very nearly correct ; while number 6 is too high. In Roscoe and Schorlemmer's *Treatise on Chemistry*, Vol. I, page 538, I find that no less a man than Wöhler directs that the sulphide of arsenic obtained in *forensic work* be dissolved off the filter paper in ammonia, the resulting solution evaporated in a dish, and the element weighed as the trisulphide, As_2S_3. *No mention whatever is made of its being necessary first to dry the precipitate.* It is a very remarkable fact that the evolution of sulphuretted hydrogen during the evaporation of the ammoniacal solution should have escaped the notice of Mohr and Wöhler, and it is likewise a remarkable fact that no one has yet seen fit to call

attention to the inaccuracy involved in weighing the arsenic as the compound obtained by evaporating an ammoniacal solution of the trisulphide.

However, by following the usual method, collecting, drying and weighing on a tared paper, very satisfactory results were obtained, as the figures below given will at once show. I find it well, after a thorough washing, to remove the adhering water by means of about 10 cc. of absolute alcohol so as to hasten the subsequent drying of the precipitate. The sulphide was weighed in a very light drying-box provided with a well-fitting ground-glass stopper.

No.	St. Sol.	As_2S_3	As.	As_2O_3.	As_2O_5.
1	20 cc.	0.1935 gram.	0.1180 gram.	0.1553 gram.	0.1810 gram.
2	20	0.1930	0.1176	0.1550	0.1802
3	20	0.1940	0.1182	0.1560	0.1812

20 cc. $=$ 0.1186 gram As $=$ 0.1564 gram $As_2O_3 =$ 0.1814 gram As_2O_5. With 50 cc. H_2KAsO_4 solution I obtained 0.4869 gram $As_2S_3 =$ 0.2963 As $=$ 0.391 $As_2O_3 =$ 0.4527 As_2O_5.

I shall now return to my modification of the Holthof method of reduction.

To avoid then the large quantities of sulphurous acid necessary when working according to Holthof, and, moreover, render it possible to effect the reduction of the arsenic from the maximum to the minimum stage of oxidation in one-fourth the time hitherto considered requisite, I suggest that Holthof's method be so modified that the reduction be accomplished in hermetically sealed bottles and at a temperature equal to that of boiling water. Qualitative as well as gravimetric quantitative experiments have already proved the reduction to be fully as complete as the one proposed by Holthof, and since its advantages over the Holthof method have been clearly pointed out, it only remains for me to offer a number of test analyses, obtained under various conditions, by titrating different quantities of known solutions of reduced arsenic acid with $\frac{1}{40}$ normal iodine.

A. 1.—In making the following lot of tests the solution of H_2KAsO_4 was brought into a small bottle provided with a well-fitting ground-glass stopper, and capable of holding when filled filled 50 cc.; 20 cc. of sulphurous acid were added, the bottle was tightly stoppered and the stopper firmly tied down with a piece of stout cord. The bottle with its contents was then placed in the

briskly boiling water-bath and here permitted to remain for exactly one hour. At the end of this time the bottle containing the arsenious acid was removed from the bath, permitted to cool to such a degree that it caused no inconvenience when held in the hand, and then carefully opened. The solution was emptied into a small flask, the bottle well rinsed out with pure water and the entire liquid diluted to 150 cc. After introducing the platinum spiral, boiling down to one-half the original volume, cooling and diluting to 300 cc., the arsenic was determined by titrating with $\frac{1}{40}$ normal iodine in the manner already described.

A.—Using 5 cc. H_2KAsO_4 solution, 20 cc. sulphurous acid, and reducing as above, I obtained :

No.	St. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	A_2O_5.
I	5 cc.	15.80 cc.	0.0297 gram.	0.0392 gram.	0.0456 gram.
2	5	15.80	0.0297	0.0392	0.0456
3	5	15.65	0.0294	0.0389	0.0452
4	5	15.75	0.0296	0.0391	0.0455
5	5	15.80	0.0297	0.0392	0.0456
6	5	15.65	0.0294	0.0389	0.0452
7	5	15.80	0.0297	0.0392	0.0456
8	5	15.80	0.0297	0.0392	0.0456
9	5	15.70	0.0295	0.0390	0.0453

5 cc. $= 0.0296$ gram As $= 0.039$ gram $As_2O_3 = 0.0453$ gram As_2O_5.

2. Using 10 cc. HK_2AsO_4 solution, 20 cc. sulphurous acid, and reducing, I obtained :

No.	St. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
I	10 cc.	31.4 cc.	0.0591 gram.	0.0781 gram.	0.0907 gram.
2	10	31.5	0.0593	0.0783	0.0910
3	10	31.5	0.0593	0.0783	0.0910
4	10	31.45	0.0592	0.0782	0.0908
5	10	31.5	0.0593	0.0783	0.0910
6	10	31.4	0.0591	0.0781	0.0907

10 cc. $= 0.0593$ gram As $= 0.0782$ gram $As_2O_3 = 0.0907$ gram As_2O_5.

3. Using 20 cc. H_2KAsO_4 solution, 30 cc. sulphurous acid, and reducing, I obtained :

30

No.	St. Solu-tion.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
I	20 cc.	62.5 cc.	0.1177 gram.	0.1556 gram.	0.1805 gram.
2	20	62.7	0.1181	0.1559	0.1811
3	20	62.65	0.1180	0.1557	0.1808

20 cc. $=$ 0.1186 gram As $=$ 0.1564 gram As_2O_3 $=$ 0.1814 gram As_2O_5.

B. To test the method still further, six determinations were made with the solution containing 2.475 gram As_2O_3, as As_2O_5, in a litre. 20 cc. were used in each test, and the reduction was effected in the usual way. I obtained :

No.	St. Solu-tion.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
I	20 cc.	19.9 cc.	0.0375 gram.	0.0495 gram.	0.0575 gram.
2	20	19.8	0.0373	0.0492	0.0572
3	20	19.8	0.0373	0.0492	0.0572
4	20	19.85	0.0374	0.0493	0.0573
5	20	19.8	0.0373	0.0492	0.0572
6	20	19.8	0.0373	0.0492	0.0572

20 cc. $=$ 0.0375 gram As $=$ 0.0495 gram As_2O_3 $=$ 0.0575 gram As_2O_5.

These figures are a trifle lower than those obtained when the reduction was effected by Holthof's method. 20 cc. of the above solution should require exactly 19.9 cc. $\frac{1}{40}$ normal iodine, whereas the quantity actually used when following Holthof's directions was 20.1 cc. I have already given good reasons for believing that in this case the excess of iodine is due to organic substances which are present in the large quantities of water necessary in making a test in accordance with the first method.

Some time last year we received from a firm in Philadelphia a sample of what purported to be arsenic acid, c. p. A quantitative test proved, however, that it was in nowise chemically pure arsenic acid, but a mixture of arsenious and arsenic acids. The comparatively small precipitate obtained with magnesia mixture indicated clearly that the arsenious acid was the principal constituent. The article is in lumps, some of which, owing to their porcelain-like appearance, are immediately recognised as arsenious acid. I have examined this *so-called* arsenic acid by my modifications of the Reich and Mohr-Holthof methods, and in the following manner : A portion of the material was finely pulverised, 3.0 grams were

carefully weighed out, dissolved in a little warm caustic potash and diluted to a litre. 20 cc. were then brought into a beaker, evaporated to dryness upon the water-bath three times with fuming nitric acid, and the arsenic determined according to my last modification of the Reich process. I obtained 0.0558 gram As_2O_3, which represents the total arsenic calculated to arsenious oxide.

In the following table I give the results of six determinations of the actual amount of As_2O_3 present, each determination being made according to Mohr and with 20 cc. of the original solution :

No.	Solution.	1-40 Normal Iodine.	As_2O_3.
1	20 cc.	18.2 cc.	0.0452 gram.
2	20	18.15	0.0451
3	20	18.2	0.0452
4	20	18.2	0.0452
5	20	18.25	0.0453
6	20	18.15	0.0451

Since 20 cc. $= 0.0452$ gram, 1000 cc. $= 2.260$ grams As_2O_3, or 3.0 grams substance $= 2.26$ grams As_2O_3, which gives 75.33 per cent. As_2O_3.

The table below presents the results of six more determinations, the 20 cc. solution taken being first reduced under pressure with sulphurous acid, then boiled down one-half, and finally titrated :

No.	Solution.	1-40 Normal Iodine.	As_2O_3.
1	20 cc.	22.6 cc.	0.0562 gram.
2	20	22.6	0.0562
3	20	22.4	0.0557
4	20	22.4	0.0557
5	20	22.4	0.0557
6	20	22.4	0.0557

As present as As_2O_3, according to Reich, 0.0558 gram ; 0.0557 — 0.0452 $= 0.0105$ gram arsenious acid present as arsenic acid. Inasmuch as 99 $As_2O_3 = 115$ As_2O_5, 0.0105 gram $As_2O_3 = \dfrac{115 \times 0.0105}{99} = 0.0122$ gram As_2O_5. Since 20 cc. $= 0.0122$ gram As_2O_5, 1000 cc. $= 0.610$ gram or 3.0 grams substance $= 0.610$ gram As_2O_5, which gives 20.33 per cent. As_2O_5. The rest is undoubtedly moisture. A small sample of the substance when heated gently in a glass tube closed at one end gave quite a strong reaction for water.

In closing I would like to say that although the Mohr-Holthof method is most admirably adapted for estimating arsenic in such compounds as soluble salts, yellow and red arsenic glass, and mixtures of arsenious and arsenic oxides, for determining the element in minerals, speisses, mattes and slags, the modified Reich method is, to my mind, much to be preferred. The latter method, though possibly not so *scientifically* perfect as the former, is certainly more rapid, convenient and practical. Above all things it is singularly well suited for determining arsenic in the various kinds of metallurgical products. I have almost finished an exhaustive examination of this method, and I trust erelong to be in the position to describe the results obtained.

JOHN C. GREEN SCHOOL OF SCIENCE, *Princeton, N. Y., August* 1, 1885.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

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(Continued from p. 338.)

ANTIMONOSO-PHOSPHO-TUNGSTATES.

These salts are formed under the same conditions as the corresponding arsenoso-phospho-tungstates, and the methods of analysis to be employed are the same.

22 : 6 : 5 : 12 *Potassic Antimonoso-phospho-tungstate.*—When a solution of potassic phosphate is poured into a hot solution of sodic antimonoso-tungstate as obtained by dissolving SbOCl in 10 : 4 sodic tungstate, a very pale yellow highly crystalline salt is at once formed. This is nearly insoluble in both hot and cold water. The portion analysed was filtered off, washed upon the filter-pump with cold water, drained, and dried upon woollen paper. The salt, like many others which I have described, could not be recrystalised, but I give the results of the analyses for what they may prove to

be worth. They certainly, I think, establish the existence of the series. In this salt,

$\left\{\begin{array}{l}\text{0.7776 gram gave 0.6142 gram oxides} = 78.99 \text{ per cent.} \\ \text{0.7776 gram gave 0.4763 gram } PtCl_6K_2 = 11.90 \text{ per cent.}\end{array}\right.$

1.0323 gram gave with iodine 0.1594 gram $Sb_2O_3 = 15.44$ per cent.

0.9716 gram gave with iodine 0.1509 gram $Sb_2O_3 = 15.53$ per cent.

1.2300 gram gave 0.1805 gram $P_2O_7Mg_2 = 9.20$ per cent. P_2O_5.

1.2430 gram gave 0.1821 gram $P_2O_7Mg_2 = 9.37$ per cent. P_2O_5.

The analyses lead to the formula:

$$22WO_3.5Sb_2O_3.6P_2O_5.12K_2O + 48Aq,$$
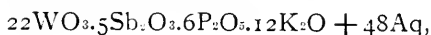
which requires

		Calculated.	Found.	
$22WO_3$	5104	54.34	54.23	
$6P_2O_5$	852	9.07	9.20	9.37
$5Sb_2O_3$	1440	15.33	15.44	15.53
$12K_2O$	1133	12.07	11.90	
$48H_2O$	864	9.19	9.13 (diff.)	
	9393	100.00		

ANTIMONIO-TUNGSTATES.

As already stated, these compounds are formed by direct oxidation of antimonoso-tungstates, one molecule of oxygen being absorbed. I shall hereafter show that, in place of oxygen, platinous chloride and other divalent compounds may serve as complex replacing molecules. Antimonio-tungstates are also formed when antimonic hydrate in excess is boiled with an acid tungstate, and when tungstic teroxide is digested or boiled with an alkaline antimonate. The salts of this series are, as a whole, not so well defined as the phospho-tungstates, vanadio-tungstates, and arsenio-tungstates, and are much more difficult to prepare in a state of purity.

Analytical Methods.—These are essentially the same as those which I have given in the case of the antimonoso-tungstates. Antimonic and tungstic oxides may be precipitated together by mercurous nitrate and mercuric oxide. In the ignited precipitate it must be assumed that the antimony is in the form of tetroxide, Sb_2O_4, and the proper correction applied, after a special determination of the antimony, as sulphide or as metal.

6 : 2 *Antimonio-tungstate of Potassium.*—This salt was prepared by boiling potassic di-antimonate for a long time with a solution of 12 : 5 acid potassic tungstate. After filtration from a small quantity of the antimonate in excess, the filtrate, on standing twenty-four hours, deposited colorless granular crystals, which were washed with cold water and dried upon woollen paper. The salt was not very soluble in water ; the crystals were soft and packed together between the fingers. In this salt,

1.0881 gram lost on ignition with WO_4Na_2 0.1076 gram $= 9.89$ per cent.

1.3566 gram lost on ignition with WO_4Na_2 0.1379 gram $=$ 10.16 per cent.

1.4636 gram gave 1.1178 gram $WO_3 + Sb_2O_4 = 76.36$ per cent.

1.3425 gram gave with KCy 0.2529 gram $Sb = 25.12$ per cent. Sb_2O_5.

0.9095 gram gave with KCy 0.1700 gram $Sb = 24.92$ per cent. Sb_2O_5.

0.8710 gram gave 0.5011 gram $PtCl_6K_2 = 11.16$ per cent. K_2O. The analyses lead to the formula

$$12WO_3.4Sb_2O_5.6K_2O + 25Aq,$$
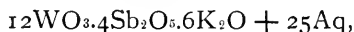
which requires :

		Calculated.	Found.	
$12WO_3$	2784	54.81	55.04	
$4Sb_2O_5$	1280	25.19	25.12	24.92
$6K_2O$	566	11.14	11.16	
$25H_2O$	450	8.86	8.91	8.64
	5080	100.00		

In calculating the results of the analysis for comparison, I have assumed that, in the ignition with the sodic tungstate to determine the water, antimonic oxide is reduced to the tetroxide Sb_2O_4 ; a correction must therefore be applied to the apparent loss. This amounts to one-twentieth of the percentage of antimonic pentoxide, and is of course to be deducted from the total loss. Chemists usually admit the existence of three classes of antimonates, corresponding respectively to metaphosphates, pyrophosphates, and orthophosphates, and formulas to support this view have been somewhat arbitrarily assigned to known compounds. If we suppose that the antimonio-tungstate above described contains

metantimonic oxide, we may write the formula as we shall write those of corresponding metaphospho-tungstates,

$$12WO_3.8SbO_2K.2K_2O + 25Aq.$$

A solution of this salt gives white crystalline precipitates with baric chloride, argentic nitrate, and cupric sulphate, and a yellow flocky-crystalline precipitate with mercurous nitrate.

ANTIMONIO–MOLYBDATES.

Salts belonging to this group are formed when freshly prepared antimonic hydrate is boiled with an acid molybdate in solution, when antimonic pentachloride in solution in chlorhydric acid is poured into a solution of an alkaline molybdate in small quantities at a time, and when molybdic oxide is digested with a solution of an alkaline antimonate.

Analytical Methods.—The separation of antimony from molybdenum cannot be effected by sulphydric acid, because molybdic sulphide is always precipitated in greater or less quantity, even when phosphoric acid is present in the solution. The only method which I have been able to devise consists in fusing the salt to be analysed or the mixture of oxides with potassic cyanide, as in the case of the separation of antimony from tungsten. In this case also it is always advisable, and sometimes necessary, to add a sufficient quantity of an alkaline carbonate to form a mixture of neutral molybdate and antimonate, as suggested by Mr. Herman Schmidt. With proper care the two oxides may be precipitated together by mercurous nitrate and mercuric oxide, and ignited without sensible loss of molybdic oxide ; but there is then always a certain amount of reduced metallic antimony present, and on the whole the method is not to be recommended.

7 : 4 : 5 *Ammonic Antimonio-molybdate.*—Antimonic hydrate dissolves readily on boiling with a strong solution of 14 : 6 ammonic molybdate. The hydrate should be in excess, and should be added in small portions at a time, until, after long boiling, a part remains undissolved. After standing twenty-four hours, beautiful colorless crystals are deposited in quantity. These have a nacreous lustre, and are readily soluble in hot water. In this salt,

1.0647 gram lost on ignition with WO_4Na_2 0.2052 gram $= 19.55$ per cent.

1.2234 gram gave 0.2418 gram $NH_4Cl = 9.60$ per cent. $(NH_4)_2O$.

0.9576 gram gave with KCy 0.3321 gram $Sb = 46.24$ per cent. Sb_2O_5.

The analyses correspond with the formula

$$7MoO_3.4Sb_2O_5.5(NH_4)_2O + 12Aq,$$
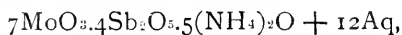
which requires:

		Calculated.	Found.
$7MoO_3$	1008	36.47	36.52
$4Sb_2O_5$	1280	46.31	46.24
$5(NH_4)_2O$	260	9.40	$\heartsuit$.60
$12H_2O$	216	7.82	7.64
	2764	100.00	

The formula may also be written

$$7MoO_3.8SbO_3NH_4.(NH_4)_2O + 12Aq.$$
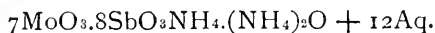
The solution of this salt gives with manganous sulphate after a time a fine canary-yellow crystalline precipitate. The ammonium salt appears to be decomposed by evaporation to dryness, or perhaps by the act of solution. The dry residue, on addition of water, leaves a white insoluble crystalline substance.

The existence of classes of vanadio-phospho-tungstates and vanadio-phospho-molybdates has already been proved. These may be embraced under the general formulas

$$mV_2O_5.nP_2O_5.pWO_3, rR'''_2O \qquad m'V_2O_5.n'P_2O_5.p'MoO_3, rR'''_2O.$$
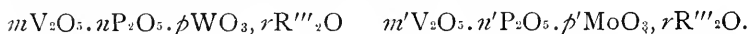
I believe that I am fully justified, though from qualitative experiments only, in maintaining that the formula

$$mR_2O_5.nR'_2O_5.pR''_2O_3 rR'''_2O$$
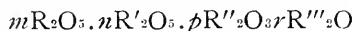
is general, and that R_2O_5 and R'_2O_5 may represent any two pentoxides, at least of the series $P_2O_5.V_2O_5.As_2O_5$ and Sb_2O_5.

PYROPHOSPHO–TUNGSTATES.

The phospho-tungstates and phospho-molybdates which have hitherto been described must be regarded as containing phosphoric oxide in the modification in which it exists in the class of tribasic or orthophosphates. This appears to be clearly shown, first, by the synthesis of these compounds from orthophosphoric acid and orthophosphates and the acid tungstates and molybdates; and, secondly, from the fact that in all cases, after the addition of an excess of ammonia, magnesia-mixture at once throws down the characteristic ammonio-magnesic orthophosphate. I shall now show that the other modifications of phosphoric oxide or acid

enter as such into similar compounds, so that we have perfectly well defined groups of pyrophospho-tungstates, metaphospho-tungstates, etc., and corresponding compounds containing molybdenum; and that, in the compounds so formed, the various modifications of phosphoric oxide preserve as it were their individuality. I shall further render it at least probable that there are groups—of phospho-tungstates for instance—in which two different modifications of phosphoric oxide may exist, each preserving its own characteristic properties. I do not now assert that in each of the complex groups which I have described ortho-phosphoric acid may be replaced by some other modification. That remains for experimental investigation. It is at least clear that the field already opened for study is one of practically unlimited extent, as even an elementary application of the algebraical theory of permutations and combinations will show.

Pyrophospho-tungstates are formed when tungstic hydrate or tungstic oxide which has not been ignited is boiled with an alkaline pyrophosphate. The oxide readily dissolves, usually forming a yellow liquid. It is best to employ sodic pyrophosphate, as this gives a much more soluble salt, but the pyrophosphate must be specially prepared in the laboratory, and the tungstic oxide should be in excess. Neutral salts of the heavy metals usually give precipitates in solutions of the alkaline pyrophospho-tungstates; these precipitates are not necessarily salts of the same group, but are very often at least either pyrophosphates of the metallic bases or double pyrophosphates of the metal and of sodium or potassium.

Analytical Methods.—These are the same as those which I have employed in the case of the orthophospho-tungstates, only in the determination of the phosphoric oxide it is necessary to evaporate the salt two or three times in succession to dryness with an excess of chlorhydric acid, so as to convert the phosphoric acid present completely into the ortho or tribasic form. In the absence of any standard of comparison, it is necessary to speak with much hesitation, but it has always appeared to me that in these salts—in other words, in the presence of tungstic oxide—the conversion of pyrophosphoric acid into orthophosphoric acid is more difficult, or at least takes place more slowly, than in the case of the ordinary pyrophosphates. Tungstic and phosphoric oxides may in these compounds also be precipitated together by mercurous nitrate and mercuric oxide.

22 : 3 : 6 *Ammonio-sodic Pyrophospho-tungstate.*—A boiling solution of sodic pyrophosphate readily dissolves tungstic oxide as prepared by the action of chlorhydric or nitric acid upon calcic tungstate, but not ignited. The filtrate has a dull yellow color, and gives with a strong solution of ammonic chloride an abundant white crystalline precipitate, which cannot be purified by recrystallisation, but which may be well washed upon the filter-pump with cold water, in which it is soluble to a very small extent. Hot water in large excess dissolves it, but even cold ammonia water dissolves it with much difficulty. When boiled for a long time with a solution of mercurous nitrate, the salt gives at first a white and finally a yellow mercurous salt. Argentic nitrate in solution gives at first with the salt extremely minute talcose scales, but on boiling for some time the whole dissolves to a clear liquid. When the salt is boiled with a solution of baric chloride, a flocky-crystalline white baric salt is formed. Cupric sulphate on boiling dissolves the pyrophospho-tungstate, but on cooling a pale green crystalline body separates, which does not contain tungsten. The salt, precipitated by ammonic chloride as above, after washing with cold water and drying upon woollen paper, was analysed :

0.6626 gram lost on ignition 0.1060 gram $= 16.00$ NH_3 and H_2O.

0.9866 gram gave 0.2479 gram $P_2O_7Mg_2 = 16.07$ per cent. P_2O_5.
0.5488 gram gave 0.0499 gram $(NH_4)_2O = 9.09$ per cent.

0.8188 gram gave 0.6504 gram oxides $= 79.46$ per cent. WO_3 and P_2O_5.

In determining the phosphoric oxide, the salt was several times in succession evaporated to dryness with nitric acid.

The analyses agree with the formula

$$22WO_3.3[P_2O_7Na_4]6[P_2O_7(NH_4)_4]2(NH_4)_2O + 31Aq,$$
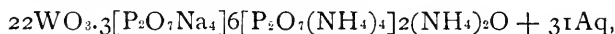
which requires :

		Calculated.	Found.
$22WO_3$	5104	63.48	63.39
$9P_2O_5$	1278	15.90	16.07
$6Na_2O$	372	4.63	4.54 (diff.)
$14(NH_4)_2O$	728	9.06	9.09
$31H_2O$	558	6.93	6.91
	8040	100.00	

As already stated, the salt is dissolved by a large excess of hot water to a clear colorless solution. Cupric sulphate gives in this solution a pale blue crystalline precipitate of a pyrophosphate free from tungstic oxide. Argentic nitrate and baric chloride give white flocky-crystalline precipitates. Either, therefore, the salt is decomposed by solution or by the action of cupric sulphate.

22 : 9 : 18 *Potassic Pyrophospho-tungstate.* — When potassic bromide and acetic acid are added to the saturated solution of tungstic oxide in sodic pyrophosphate, a white granular fine-grained crystalline precipitate very slightly soluble in cold water is formed at once. For analysis the salt was washed upon the filter-pump with cold water, and dried on woollen paper. In this salt,

0.9440 gram gave 0.6717 gram oxides $= 71.15$ per cent. WO_3 and P_2O_5.

1.3647 gram gave 0.9721 gram oxides $= 71.23$ per cent. WO_3 and P_2O_5.

0.9070 gram gave 0.2015 gram $P_2O_7Mg_2 = 14.21$ per cent. P_2O_5.
0.9817 gram lost 0.0960 gram $H_2O = 9.78$ per cent.

The phosphoric oxide was determined as before by evaporation with nitric acid to convert the pyrophosphoric into orthophosphoric acid.

The analyses correspond to the formula

$$22WO_3.9P_2O_7K_4 + 49Aq,$$
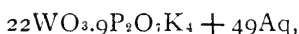
which requires :

		Calculated.	Found.	
$22WO_3$	5104	56.94	56.94	57.02
$9P_2O_5$	1278	14.26	14.21	
$18K_2O$	1699	18.96	19.07	
$49H_2O$	882	9.84	9.78	
	8963	100.00		

22 : 9 : 13 *Potassic Pyrophospho-tungstate.* — This salt was obtained by boiling tungstic oxide for some time with potassic pyrophosphate. After filtration and standing a white crystalline salt separated, which was well drained on the filter-pump, and then washed with cold water in which it is but slightly soluble. In much boiling water it dissolves on boiling to a clear liquid. The solution gives a white crystalline precipitate with argentic

nitrate—no precipitate at first with cupric sulphate. On boiling, a very pale blue crystalline salt separates, which does not contain tungsten, and is either a cupric pyrophosphate or a double salt of potassium and copper. The solution of the pyrophospho-tung-state gives a dense white distinctly crystalline precipitate with mer-curous nitrate, and a turbid solution with baric chloride yielding on boiling a white feathery crystalline salt. No precipitate is formed with manganous sulphate, but after a short time the solution becomes turbid. In this salt,

1 6112 gram gave 1.2119 gram oxides = 75.22 per cent.

1.9796 gram gave 1.4894 gram oxides = 75.23 per cent.

1.6421 gram gave 0.3862 gram $P_2O_7Mg_2$ = 15.06 per cent.

1.2433 gram lost by direct ignition 0.1299 gram = 10.45 per cent.

The analyses agree closely with the formula

$$22WO_3.6P_2O_7K_4.3P_2O_7H_4.K_2O.H_2O + 42Aq,$$
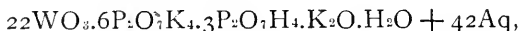
so that the type is, as in other cases,

$$22WO_3.9P_2O_7H_4.2R_2O.$$
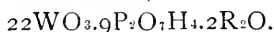
The formula requires :

		Calculated.	Found.	
$22WO_3$	5104	60.11	60.17	60.18
$9P_2O_5$	1278	15.05	15.05	
$13K_2O$	1227	14.45	14.32 (diff.)	
$49H_2O$	882	10.39	10.45	
	8491	100.00		

All the compounds of this group which I have obtained belong, as will be seen, to the same type which contains the frequently recurring chemical mass of twenty-two molecules of tungstic oxide, united to nine molecules of pyrophosphoric acid or a pyrophos-phate, together with a certain amount of base over and above that required to saturate the phosphoric oxide. We may represent this group provisionally by a structural formula containing *nine* groups of the form :

$$\begin{matrix} HO \\ HO \end{matrix} \Big> PO-O-OP \Big< \begin{matrix} OH \\ OH \end{matrix}$$
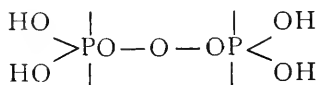
Further investigation will doubtless show that there are other series of pyrophospho-tungstates and analogous pyrophospho-

molybdates. It is especially desirable to study the compounds which remain in solution after the precipitation of part of the pyrophosphoric oxide by means of cupric sulphate.

It may here be remarked, that Wallroth[1] has described a series of pyrophosphates which contain *nine* molecules of P_2O_7, united in each case to thirty-six atoms of metal. Thus we have

$$Ca_{10}Na_{16}(P_2O_7)_9$$
$$Mg_{10}Na_{16}(P_2O_7)_9$$
$$Co_{10}Na_{16}(P_2O_7)_9$$
$$Ni_{10}Na_{16}(P_2O_7)_9.$$
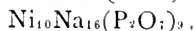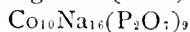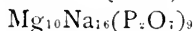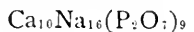
It would therefore appear that similar complex molecules enter directly into combination with twenty-two molecules of tungstic oxide, but that the complexity is not necessarily due to a determining action on the part of the latter.

MONOMETAPHOSPHO–TUNGSTATES.

In preparing the salts of this series I have employed ordinary glacial phosphoric acid, which, according to Brescius,[2] contains about 50 per cent. of sodic metaphosphate, and which may be regarded as a mixture of sodic metaphosphate and metaphosphoric acid. I have assumed that the acid is here in the form of monometaphosphoric acid, although upon this point the evidence is still insufficient. As the relations of metaphosphoric acid to indicators of various kinds have not hitherto been studied, the following brief note may be of interest. A solution of glacial phosphoric acid is neutral to tropæolin. The same solution required for equal volumes with purpurin 23 cc. sodic hydrate solution; with hæmatoxylin, 14 cc.; and with alizarin, 12.5 cc. No definite end reaction could be obtained with phenol-phthalein, methyl-orange or rosolic acid.

Monometaphospho-tungstates are formed by the direct action of the acid upon acid tungstates. They are, frequently at least, gummy uncrystalline bodies. When crystalline the crystals are usually soft, and pack together readily. The salts of the alkaline earths are usually more or less distinctly crystalline. Those of the heavy metallic oxides are often pasty, and sometimes oily. They are not very readily converted into orthophospho-tungstates, and in this respect they seem to differ materially from the corresponding metaphospho-molybdates.

[1] Bull. de la Soc. Chimique [2], **39**, 316.   [2] Zeitschrift für analytische Chemie **6**, 187.

Analytical Methods.—In these salts tungstic and metaphosphoric oxides may be precipitated together by mercurous nitrate and mercuric oxide. Metaphosphoric acid may be converted into orthophosphoric acid by dissolving the salt in the least possible quantity of water, adding strong sulphuric acid, evaporating the solution nearly to dryness, and repeating this process several times. This method is very much better than fusion with alkaline carbonates, which effects the transformation of metaphosphoric acid in a very imperfect manner. I believe that I can assert with entire confidence, that in the class of monometaphospho-tungstates the conversion of the metaphosphoric into orthophosphoric acid is much more difficult than in the metaphosphates. The precipitation of the orthophosphoric acid by magnesia mixture must of course be repeated twice.

24:2:3 *Potassic Monometaphospho-tungstate.*—When a cold freshly prepared solution of glacial phosphoric acid is digested with 10:4 potassic tungstate, part of this salt dissolves, while the undissolved portion changes its character, and is converted into a soft crystalline, very slightly soluble mass. This may be filtered off and washed with cold water. In this salt,

$\left\{\begin{array}{l}\text{1.5236 gram lost on ignition 0.0857 gram} = 5.63 \text{ per cent. } H_2O.\\ \text{1.5236 gram gave 0.0517 gram } P_2O_7Mg_2 = 1.96 \text{ per cent. } P_2O_5.\end{array}\right.$
0.9934 gram gave 0.0303 gram $P_2O_7Mg_2 = 2.17$ per cent. P_2O_5.
1.0686 gram gave 0.0352 gram $P_2O_7Mg_2 = 2.11$ per cent. P_2O_6.
$\left\{\begin{array}{l}\text{1.1490 gram gave 1.0171 gram oxides} = 88.52 \text{ per cent.}\\ \text{1.1490 gram gave 0.3327 gram } PtCl_6K_2 = 5.70 \text{ } K_2O.\end{array}\right.$

The anlyses correspond very well to the formula

$$24WO_3.2[PO_3K]_3K_2O + 20Aq,$$
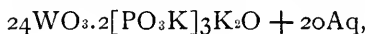
which requires :

		Calculated.		Found.	
$24WO_3$	5568	86.36		86.38	
P_2O_5	142	2.21	2.11	2.17	1.96
$4K_2O$	376	5.84		5.70	5.85 (diff.)
$20H_2O$	360	5.59		5.63	
	6446	100.00			

The filtrate from the 24 : 2 salt, on standing, deposits a white crystalline salt, which, when thrown on a filter and washed with cold water, presents a colorless gummy mass. Of this salt,

0.6183 gram gave 0.0307 gram $P_2O_7Mg_2 = 3.17$ per cent. P_2O_5.

{ 0.8173 gram gave 0.6844 gram oxides $= 83.72$ per cent.
{ 0.8173 gram lost on ignition 0.0607 gram $= 7.43$ per cent.

From an oversight, the potassic oxide was not determined in this salt, which may be either

$$16WO_3.2[PO_3K]2K_2O.2Na_2O + 20Aq,$$

or

$$16WO_3.2[PO_3K]5Na_2O + 20Aq.$$
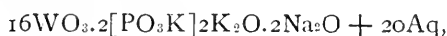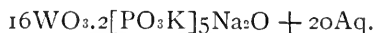
The formulas require, respectively,

		Calc'd.	Found.	Calc'd.		
$16WO_3$	3712	80.34	80.56	80.38	3712	$16WO_3$
P_2O_5	142	3.07	3.17	3.07	142	P_2O_5
$3K_2O$	283	6.12 } 8.80	8.87	2.04 } 8.76	94	K_2O
$2Na_2O$	124	2.68 }		6.72 }	310	$5Na_2O$
$20H_2O$	360	7.79	7.40	7.79	360	$20H_2O$
	4621	100.00		100.00	4618	

$18:1:2$ *Ammonic Monometaphospho-tungstate.*—When $12:5$ ammonic tungstate is boiled with a solution of glacial phosphoric acid, a white crystalline mass remains undissolved, very different in appearance from the ammonic tungstate employed. This salt requires a large quantity of boiling water for solution, but is only slightly soluble in cold water. For analysis, it was thoroughly drained upon the filter-pump, and then washed with cold water. Of this salt,

1.6896 gram lost by ignition with WO_4Na_2 0.1082 gram $= 6.40$ per cent.

1.5026 gram gave 0.0745 gram $P_2O_7Mg_2 = 3.17$ per cent. P_2O_5.

1.4267 gram gave 0.0316 gram $(NH_4)_2O = 2.21$ per cent.

The analyses correspond to the formula

$$18WO_3.2[PO_3NH_4].(NH_4)_2O + 11Aq,$$
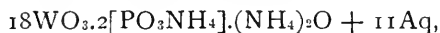
which requires:

		Calculated.	Found.
$18WO_3$	4176	90.39	90.43
P_2O_5	142	3.08	3.17
$2(NH_4)_2O$	104	2.25	2.21
$11H_2O$	198	4.28	4.19
	4620	100.00	

The filtrate from this salt gives on evaporation a thick colorless syrup, in which white crystals—perhaps of the salt above described —were suspended. It will be seen that the action of PO_3H upon $12:5$ ammonic tungstate is essentially the same as upon the $10:4$ potassic salt, and that in each case at least one crystalline and one gummy salt are formed.

The analyses given are sufficient to establish the existence of three classes of monometaphospho-tungstates. My work on this subject is to be regarded merely as preliminary, and is intended to direct the attention of other chemists to this class of salts. In another paper I shall give the results of a more detailed study of the various metaphospho-tungstates. Fleitmann and Henneberg have described five series of metaphosphates; in addition to these, there remain to be studied, in their relation to tungstic and molybdic oxides, the two series of tetraphosphates, $P_4O_7.6RO$ and dekaphosphates, $P_{10}O_{19}.12RO$, discovered by the same chemists, as well as the new group of salts described by Salzer,[1] which may be called hypophosphates.

ORTHOMETAPHOSPHO-TUNGSTATES.

A single salt of this series will be sufficient to establish the existence of compounds into which two different modifications of phosphoric acid enter, to a certain extent at least preserving their peculiar characteristics.

$22:6:11:7$ *Potassio-sodic Orthometaphospho-tungstate.*—When $24:1$ sodic phospho-tungstate is boiled with a solution of sodic monometaphosphate, PO_3Na, the salt dissolves readily to a clear liquid. Potassic bromide gives a white precipitate in this solution. After filtering and washing with cold water, a white gelatinous mass remains upon the filter, but slightly soluble in water. Of this salt,

1.2008 gram gave 0.8728 gram oxides $= 72.68$ per cent.

1.5959 gram gave 0.1611 gram oxides $= 72.76$ per cent.

1.3558 gram gave 0.2220 gram $P_2O_7Mg_2 = 10.47$ per cent. P_2O_5.

0.8822 gram gave 0.5774 gram $PtCl_6K_2 = 12.70$ per cent. K_2O.

1.4517 gram lost on ignition with WO_4Na_2 0.1349 gram $= 9.29$ per cent.

The analyses correspond with the formula

$$22WO_3.6P_2O_5.11K_2O.7Na_2O + 42Aq,$$
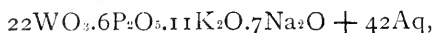
[1] Pharmaceutische Zeitung, Bunzlau, 1881. Ann. der Chemie, **211**, 1.

which requires:

		Calculated.	Found.
$22WO_3$	5104	62.36	62.25
$6P_2O_5$	852	10.41	10.47
$11K_2O$	1038	12.68	12.70
$7Na_2O$	434	5.31	5.29
$42H_2O$	756	9.24	9.29
	8184	100.00	

The solution of this salt in chlorhydric acid gives, with magnesia-mixture and ammonia, a precipitate which appears to contain ammonio-magnesic phosphate and magnesic metaphosphate. It is of course possible that a portion of the metaphosphoric acid may have been converted into orthophosphoric acid by the act of solution in chlorhydric acid. I know of no method by which really reliable determinations, either qualitative or quantitative, can be made in compounds of this kind. In the analysis above, the salt was evaporated several times with strong sulphuric acid, and the phosphoric acid then determined with magnesia-mixture. The total quantity of base in the salt is exactly sufficient to saturate six molecules of orthophosphoric acid, but the salt certainly contains at least a part of the phosphorus as metaphosphoric oxide. We may perhaps assume that the two modifications are equally divided between the bases, and the formula may be then written

$$22WO_3.3(P_2O_5.3K_2O).6PO_3Na.2K_2O.4Na_2O + 42Aq.$$
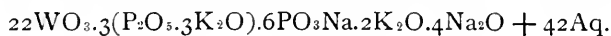
The subject of course requires further investigation.

MONOMETAPHOSPHO-MOLYBDATES.

The salts belonging to this series appear also to belong to two different classes, which may be simply distinguished as crystalline and gummy salts. Both these classes are readily converted by acids into orthophospho-molybdates. Up to the present time I have made only a preliminary study of these compounds.

10 : 2 : 5 *Ammonic Monometaphospho-molybdate.*—When glacial phosphoric acid is neutralised with ammonia, and the solution is mixed with one of 14 : 6 ammonic molybdate, no precipitate is formed, but on evaporation a thick, nearly colorless gummy mass is formed. On standing for some time, this is almost completely converted into a crystalline mass. This may be drained, redis-

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solved in water, in which it is very soluble, and recrystallised several times from very concentrated solutions. It then presents very beautiful, perfectly colorless, flat tabular crystals. The solution gives at once, with nitric acid, a precipitate of yellow orthophospho-molybdate; with magnesia-mixture and ammonia, a precipitate very different from ammonio-magnesic orthophosphate. Argentic nitrate gives a flocky-crystalline precipitate; baric and thallous nitrates give beautiful white feathery-crystalline salts; mercurous nitrate gives a pale flocky-crystalline precipitate, while cuprous sulphate forms none. Of this salt,

1.4314 gram gave 0.3002 gram $P_2O_7Mg_2 = 13.41$ per cent. P_2O_5.

0.8385 gram gave 0.1022 gram $(NH_4)_2O = 12.19$ per cent.

1.4016 gram lost 0.2776 gram $= 19.81$ per cent.

The analyses agree with the formula
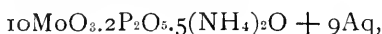
$$10MoO_3.2P_2O_5.5(NH_4)_2O + 9Aq,$$

which requires :

		Calculated.	Found.
$10Mo_2O_3$	1440	$\left. \begin{array}{l} 67.10 \\ 13.23 \end{array} \right\} 80.33$	$\left. \begin{array}{l} 66.78 \\ 13.41 \end{array} \right\} 80.19$
$2P_2O_5$	284		
$5(NH_4)_2O$	260	12.12	12.19
$9H_2O$	162	7.55	7.62
	2146	100.00	

The formula may be more advantageously written

$$10MoO_3.4[PO_3NH_4].3(NH_4)_2O + 9Aq.$$
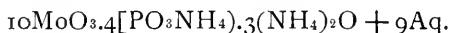
Empirically, this salt has, except as regards water of crystallisation, the same formula as the acid 10 : 2 orthophospho-molybdate, which I have already described.

HEXAMETAPHOSPHO-MOLYBDATES.

The single salt of this series which I have thus far obtained will serve as an example, and I hope as an incentive to further study.

14 : 3 : 4 *Baric Hexametaphospho-molybdate.*—Sodic hexametaphosphate, obtained by heating the so-called microcosmic salt until a clear colorless glass is obtained, gives a white colorless crystalline salt with baric chloride, which, after washing with cold water, readily dissolves in an excess of a solution of 14 : 6 ammonic

molybdate. After a short time the clear filtered solution deposits an abundance of beautiful colorless acicular crystals. This salt cannot be perfectly decomposed by boiling with a solution of mercurous nitrate. Nitric acid dissolves it to a turbid liquid, with formation of a yellow powder. After boiling with the acid, ammonic molybdate gives the characteristic yellow crystalline precipitate, indicating the presence of orthophosphoric acid. Of this salt,

1.0140 gram lost on ignition with WO_4Na_2 0.2463 gram $= 24.31$ per cent.

1.8970 gram gave 0.4286 gram $SO_4Ba = 14.84$ per cent. BaO.

2.0403 grams gave 0.3454 gram $P_2O_7Mg_2 = 10.83$ per cent. P_2O_5.

The formula appears to be

$$14MoO_3.3P_2O_5,4BaO + 55Aq,$$
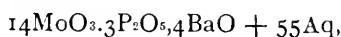
which requires:

		Calculated.	Found.
$14MoO_3$	2016	49.86	50.02
$3P_2O_5$	426	10.53	10.83
$4BaO$	612	15.13	14.84
$55H_2O$	990	24.48	24.31
	4044	100.00	

I give this formula with much reserve, and only as probably correct. To express the presence of hexametaphosphoric oxide it may be written

$$14MoO_3.[Ba_3.6PO_3].BaO + 55Aq.$$

I shall return to the subject at another time.

<div align="center">STANNO-PHOSPHO-TUNGSTATES.</div>

The vanadico-vanadio-tungstates and vanadico-vanadio-molybdates which I have described furnish instances of compounds embraced under the general formulas

$$mRO_3.nR'O_2.pR''_2O_5.rR'''_2O.$$
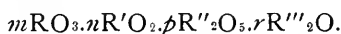
I shall show that the compounds belonging to this type are very numerous, and frequently very well defined. For the present, it will be sufficient to cite two new series of hitherto undescribed salts, my object being to direct the attention of other chemists to a

new field of investigation, and to point out methods of preparation and of analysis which may facilitate their work.

Stanno-phospho-tungstates are formed when the stanno-chlorides of ammonium or of the alkaline metals are mixed in solution with acid alkaline phospho-tungstates. They are colorless crystalline salts, so far as studied. As a representative of this series we may take the ammonium salt.

Analytical Methods.—In these salts the three higher oxides may be determined together by precipitation with mercurous nitrate and mercuric oxide, but the ignited oxides should be evaporated once or twice with nitric acid to oxidize any reduced tin. Tin may be separated as metal by fusion with potassic cyanide, and phosphoric oxide may be determined after separating tin with sulphydric acid.

22 : 2 : 1 : 2 *Ammonic Stanno-phospho-tungstate.*—When a solution of stanno-chloride of ammonium is poured into a clear cold solution of 24 : 1 sodic phospho-tungstate $(24WO_3.P_2O_5.2Na_2O + 27Aq)$, a beautiful white crystalline precipitate is formed at once. This is but slightly soluble in boiling water. By long boiling with baric chloride, argentic nitrate, or mercurous nitrate, the salt gives crystalline compounds, which in the cases of the barium and silver salts are colorless; in that of the mercurous salt, yellow. So far as can be determined without quantitative analyses, there appears to be in these cases only a simple double decomposition. For analysis the ammonium salt was thoroughly washed with cold water on the filter-pump, drained, and dried on woollen paper. Of this salt,

1.3577 gram lost on ignition with WO_4Na_2 0.0833 gram $= 6.14$ per cent.

1.2921 gram lost on ignition without WO_4Na_2 0.0811 gram $= 6.29$ per cent.

1.6822 gram gave 0.0646 gram $Sn = 4.88$ per cent. SnO_2.

1.1596 gram gave 1,0850 gram oxides $= 93.57$ per cent.

1.1826 gram gave 0.0443 gram $P_2O_7Mg_2 = 2.39$ per cent.

0.9575 gram gave 0.0182 gram $(NH_4)_2O = 1.89$ per cent.

The analyses correspond well with the formula

$$22WO_3.2SnO_2.P_2O_5.2(NH_4)_2O + 15Aq,$$
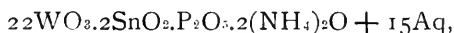
which requires :

22WO₃	5104	86.21	86.30
2SnO₂	300	5.06	4.88
P₂O₅	142	2.39	2.39
2(NH₄)₂O	104	1.75	1.89
15H₂O	270	4.59	4.24
	5920	100.00	99.70

STANNO-PHOSPHO-MOLYBDATES.

The salts of this series are formed under precisely the same conditions as the corresponding stanno-phospho-tungstates. It is at least probable that it will be found that the two classes of salts may be formed under other conditions, as, for example, by boiling stannic oxide with phospho-tungstates and phospho-molybdates, or by digesting stanno-tungstates and stanno-molybdates with alkaline phosphates or with phosphoric acid; but I have made no experiments to determine these points.

Analytical Methods.—Tin may be determined in these salts by fusion with potassic cyanide, provided that, as in the case of the separation of antimony from tungsten and from molybdenum, a sufficient quantity of an alkaline carbonate is added to convert all the higher oxides present into neutral salts. Under these circumstances, no insoluble compound of molybdenum is formed, and the tin separates in bright metallic globules. Phosphoric acid may be determined in these salts after separating the whole of the tin and the greater part of the molybdenum by means of sulphydric acid. Molybdic oxide is estimated most advantageously by difference.

16 : 4 : 3 : 3 *Ammonic-Stanno-phospho-molybdate.*—When a solution of stanno-chloride of ammonium, $SnCl_6(NH_4)_2$, is poured into a hot solution of acid ammonic phospho-molybdate.

$$10MoO_3 . 2P_2O_5 . 5(NH_4)_2O + 7Aq,$$
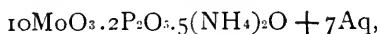
a fine bright yellow crystalline precipitate is formed, which quickly settles and leaves a colorless solution. The salt is almost insoluble, even in boiling water, and may perhaps find an application in the separation and quantitative estimation of tin. On boiling with mercurous nitrate it gives a buff-yellow crystalline mercurous salt. Under the same circumstances cupric sulphate yields yellowish-

green crystals, and argentic nitrate a very pale yellow, not distinctly crystalline salt. An excess of ammonia readily decomposes the salt with separation of a white gelatinous mass. Of this salt,

0.8648 gram gave 0.1023 gram metallic tin $=$ 15.18 per cent. SnO_2.

2.3780 grams gave 0.3865 gram $P_2O_7Mg_2 =$ 10.40 per cent. P_2O_5.

1.2021 gram gave 0.2016 gram $P_2O_7Mg_2 =$ 10.73 per cent. P_2O_5.

1.0130 gram gave 0.3839 gram $(NH_4)_2O =$ 3.79 per cent.

1.7170 gram lost on ignition 0.2793 gram $=$ 16.27 per cent.

The analyses give the formula

$$16MoO_3 . 4SnO_2 . 3P_2O_5 . 3(NH_4)_2 + 28Aq,$$

which requires

		Calculated.	Found.
$16MoO_3$	2304	57.75	57.97 (diff.)
$4SnO_2$	600	15.04	15.19
$3P_2O_5$	426	10.67	10.73 10.40
$3(NH_4)_2O$	156	3.91	3.79
$28H_2O$	504	12.63	12.48
	3990	100.00	

ALUMINO–MOLYBDATES.

Heinrich Struve,[1] in 1854, described a remarkable series of salts, which he regarded simply as double molybdates of the sesquioxides of aluminum, iron, manganese, chromium, and ammonia, potash, or soda. These salts were embraced under two different types, particular aluminic, ferric, and chromic salts, having respectively the formulas

$$Al_2O_3.6MoO_3 + 3(K_2O.2MoO_3) + 20Aq.$$
$$Fe_2O_3.6MoO_3 + 3(K_2O.2MoO_3) + 20Aq.$$
$$Cr_2O_3.6MoO_3 + 3(Na_2O.2MoO_3) + 21Aq.$$
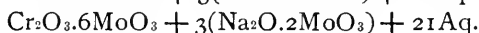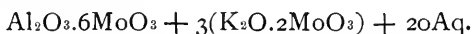
The manganic salt, on the other hand, was represented by

$$Mn_2O_3.6Mo_3 + 5(K_2O.2MoO_3) + 12Aq.$$

Parmentier[2] has recently added a new term to this series, the type being

$$R_2O_3.10MoO_3.2R'_2O + xAq.$$
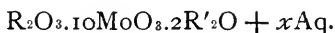
[1] Petersburg Acad. Bull., **12**, 142.   [2] Comptes Rendus, **95**, 839.

The true character of these compounds could not be understood at the time of their discovery. I find that in solutions of the salts described by Struve, potassium or ammonium may be directly replaced by other metals or by alkaloids,—a fact which was, however, noticed by Struve himself. In addition,—and this is of more importance,—I find that there are series which contain the sesquioxides named with phosphoric and molybdic oxides, so that we have classes of ferro-phospho-molybdates, etc. From my point of view, the compounds in question may be classed under three types, of which the following will serve as representatives :

Alumino-dodeka-molybdates, $Al_2O_3.12MoO_3.6R_2O$.

Ferrico-dodeka-molybdates, $Fe_2O_3.12MoO_3.6R_2O$.

Chromico-dodeka-molybdates, $C_{22}O_3.12MoO_2.6R_2O$.

Manganico-hekkaideka-molybdates, $Mn_2O_3.16MoO_3.5K_2O.H_2O + 11Aq$.

Alumino-deka-molybdates, $Al_2O_3.10MoO_3.2R_2O$.

Ferrico-deka-molybdates, $Fe_2O_3.10MoO_3.2R_2O$.

Chromico-deka-molybdates, $Cr_2O_3.10MoO_3.2R_2O$.

All these classes of salts containing oxides corresponding to chlorides of the type R_2Cl_6 are very much less stable than compounds containing oxides of the types R_2O_5, RO_2, and R_2O_3 (corresponding to chlorides RCl_3). We may assume provisionally that the component

$$\begin{array}{c} | \\ R = O \\ | \\ O \\ | \\ R = O \\ | \end{array}$$
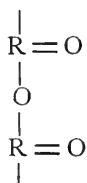
enters into the structural formulas which represent this class of compounds. Struve states that he has obtained similar compounds containing tungsten, but these have not been described.

Klein[1] has carefully studied four series of boro-tungstates, embraced respectively under the general formulas

$$7WO_3.B_2O_3.2R_2O$$
$$9WO_3.B_2O_3.2R_2O$$
$$12WO_3.B_2O_3.4R_2O$$
$$14WO_3.B_2O_3.3R_2O.$$
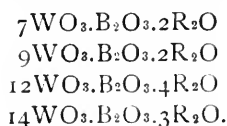
[1] Bull. de la Société Chim. [2,] **36**, 547, **37**, 202.

Since boron is the lowest term in the third column of the periodic series, aluminum being the next higher, it would seem probable that the oxides which correspond to still higher terms in the same column will form similar compounds. Chromium, manganese, iron, nickel, and cobalt may be regarded as higher harmonics of aluminum, and at least three of these form analogous series. It still remains to study the relations of the oxides of the cerium and yttrium groups to molybdic and tungstic oxides, since these correspond to chlorides of the type RCl_3, and yet differ in a very marked degree from oxides like As_2O_3, Sb_2O_3, etc. I have made some progress in this investigation and will in another paper give my results in detail.

GENERAL–CONCLUSIONS.

The formulas and details which I have given in the present instalment of my work appear to justify the following general conclusions.

1. Vanadic pentoxide unites with phosphoric or arsenic pentoxides in various proportions to form well-defined complex acids. In some, at least, of these, we seem to have series in which vanadic pentoxide plays the same part as tungstic or molybdic teroxide, or, in other words, appears to enter the compound as $V_2O_2.O_3$.

2. Compounds of vanadic pentoxide, vanadic dioxide, and phosphoric or arsenic pentoxide, may be formed, possessing properties analogous to those of the compounds of tungstic or molybdic teroxides with pentoxides and dioxides.

3. The series of oxides P_2O_3, As_2O_3, Sb_2O_3, unite with tungstic and molybdic oxide to form well-defined series of complex acids. In these the ratio of the number of molecules of the oxides of the types R_2O_3 and MO_3 is much lower than in the cases of the compounds which contain orthophosphoric or ortho-arsenic acids.

4. Compounds exist which contain one oxide of the R_2O_3 (or RO_3H_3) and one of the type R'_2O_5 united to tungstic or molybdic oxide, the general formula being

$$mMO_3.nR_2O_3.pR'_2O_5.rR''_2O.$$
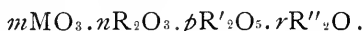
5. Compounds exist which contain acids of the types RO_2H_3 (hypo-phosphorous acid, for instance) and R'_2O_5 united to tungstic or molybdic oxides, the general formula being

$$mMO_3.nRO_2H_3.pR'_2O_5.rR''_2O.$$
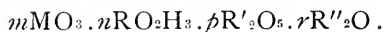
6. Classes of compounds exist which contain oxides of the types RO_2 and R'_2O_5 united to tungstic or molybdic oxides, the general formula being

$$mMO_3 . nRO_2 . pR'_2O_5 . rR_2O ,$$
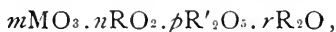
where, as in the other general formulas, M represents either tungsten or molybdenum.

7. Compounds exist which contain pyrophosphoric and metaphosphoric acids in place of orthophosphoric acid. So far as it is possible to judge from the salts analysed, these contain, or at least may contain, phosphoric and tungstic or molybdic oxides in a lower ratio to each other than in the ortho-phospho-compounds.

8. Complex acids exist which contain two different modifications of phosphoric acid, as, for instance, metaphosphoric and orthophosphoric acids or oxides.

9. The salts described by Struve and by Parmentier establish the existence of a class of complex acids, which contain oxides of the type R_2O_3, corresponding to chlorides of the type R_2Cl_6. The true character of these salts is for the first time recognized.

Partly for convenience of reference, and partly to show as distinctly as possible the extent and richness of the field of investigation now opened, I have collected all the formulas of the last and present instalments of my work, prefixing the mark † to those which are in my judgment less certainly established. ·

Phospho-vanadates.
$P_2O_5.V_2O_5.(NH_4)_2O + Aq.$
$P_2O_5.V_2O_5.2Ag_2O + 5Aq.$
$P_2O_5.2V_2O_5.(NH_4)_2O + 7Aq.$
$4 P_2O_5.6V_2O_5.3K_2O + 21Aq.$
$7 P_2O_5.6V_2O_5.3H_2O + 34Aq.$
$20 V_2O_5.P_2O_5.3H_2O + 56Aq.$

Arsenio-vanadates.
$5As_2O_5.8V_2O_5.3H_2O + 24Aq.$
† $7As_2O_5.6V_2O_5.3H_2O.$

Phospho-vanadico-vanadates.
$18V_2O_5.VO_2.2P_2O_5.7(NH_4)_2O + 50Aq.$
† $4V_2O_5.VO_2.5P_2O_5.4Na_2O + 37Aq.$
$12P_2O_5.12VO_2.6V_2O_5.5K_2O + 40Aq.$
$12P_2O_5.14VO_2.6V_2O_5.7K_2O + 52Aq.$
$14P_2O_5.16VO_2.6V_2O_5.7(NH_4)_2O + 67Aq.$
$10P_2O_5.11VO_2.5V_2O_5.5(NH_4)_2O + 41Aq.$

Arsenio-vanadico-vanadates.

$12As_2O_5.12VO_2.6V_2O_5.5(NH_4)_2O + 7Aq.$
$9As_2O_5.9VO_2.8V_2O_5.4(NH_4)_2O + 11Aq.$

Vanadico-vanadates.

$4V_2O_5.2VO_2.(NH_4)_2O +'8Aq.$

Hypophospho-molybdates.

$8MoO_3.2PO_2H_3.2(NH_4)_2O + 2H_2O.$

Hypophospho-tungstates.

$18WO_3.6PO_2H_3.4K_2O + 7Aq.$

Phosphoroso-molybdates.

$24MoO_3.4PO_3H_3.4(NH_4)_2O + 17Aq.$
$24MoO_3.4PO_3H_3.4(NH_4)_2O + 25Aq.$

Phosphoroso-tungstates.

$22WO_3.4PO_3H_3.6(NH_4)_2O + 25Aq.$
$32WO_3.16PO_3H_3.5K_2O + 46Aq.$
$22WO_38PO_3H_3.2Na_2O + 25Aq.$

Arsenoso-tungstates.

$18WO_3.2As_2O_3.7(NH_4)_2O + 18Aq.$
$18WO_3.2As_2O_3.8BaO + 42Aq.$
$16WO_3.8As_2O_3.9Na_2O + 65\ Aq.$

Arsenoso-molybdates.

$8MoO_3.2As_2O_3.3BaO + 13Aq.$
$†12MoO_3.5As_2O_3(NH_4)_2O + 24Aq.$
$6MoO_3.3As_2O_3.2MnO + 6Aq.$

Antimonoso-tungstates.

$11WO_3.3Sb_2O_3.2BaO + 18Aq.$

Antimonoso-molybdates.

$17MoO_3.3Sb_2O_3.6(NH_4)_2O + 21Aq.$

Phosphoroso-phospho-tungstates.

$24WO_2.P_2O_5.2PO_3H_3.5K_2O + 13Aq.$

Phosphoroso-phospho-molybdates.

$72MoO_3.3P_2O_5.2PO_3H_3.9(NH_4)_2O + 38Aq.$

Phospho-hypophospho-tungstates.

$26WO_3.4P_2O_5.2PO_3H_3.9K_2O.Na_2O + 43Aq.$

Arsenoso-phospho-tungstates.

$32WO_3.14As_2O_3.3P_2O_5.10K_2O + 28Aq.$
$12WO_3.2As_2O_3.2P_2O_5.5K_2O.Na_2O + 15Aq.$
$60WO_3.As_2O_3.4P_2O_5.7K_2O + 55Aq.$

Arsenoso-arsenio-tungstates.

$†21WO_3.As_2O_3.4As_2O_5.10K_2O + 26Aq.$

Antimonoso-phospho-tungstates.

$22WO_3.5Sb_2O_3.6P_2O_5.12_2KO + 48Aq.$

Vanadio-molybdates.

$6MoO_3.V_2O_5.2(NH_4)_2O + 5Aq.$
$16MoO_3.2V_2O_5.5BaO + 29Aq.$
$18MoO_3.V_2O_5.8(NH_4)_2O + 15Aq.$

Vanadio-tungstates.

$5WO_3.V_2O_5.4(NH_4)_2O + 13Aq.$
$10WO_3.V_2O_5.6H_2O + 16Aq.$
$18WO_3.V_2O_5.6H_2O + 30Aq.$

Antimonio-tungstates.

$12WO_3.4Sb_2O_5.6K_2O + 25Aq.$

Antimonio-molybdates.

$7MoO_3.4Sb_2O_5.5(NH_4)_2O + 12Aq.$

Pyrophospho-tungstates.

$22WO_3.9P_2O_5.6Na_2O.14(NH_4)_2O + 31Aq.$
$22WO_3.9P_2O_5.18K_2O + 49Aq.$
$22WO_3.9P_2O_5.13K_2O + 49Aq.$

Monometaphospho-tungstates.

$†16WO_3.2[PO_3K]5Na_2O + 20Aq.$
$24WO_3.2[PO_3K]3K_2O + 20Aq.$
$18WO_3.2[PO_3NH_4](NH_4)_2O + Aq.$

Monometaphospho-tungstates.

$10MoO_3.44[PO_3NH_4].3(NH_4)_2O + 9Aq.$

Hexametaphospho-molybdates.

† $14MoO_3.[Ba_3.6PO_3].BaO + 55Aq.$

Orthometaphospho-tungstates.

$22WO_3.3[P_2O_5.3K_2O][6PO_3Na].2K_2O.2Na_2O + 42Aq.$

Phospho-vanadio-molybdates.

$48MoO_3.2P_2O_5.V_2O_5.7(NH_4)_2O + 30Aq.$
$14MoO_3.P_2O_5.8V_2O_5.8(NH_4)_2O + 50Aq.$

Phospho-vanadio-tungstates.

$60WO_3.3P_2O_5.V_2O_5.10(NH_4)_2O + 60Aq.$
$16WO_3.P_2O_5.3V_2O_5.5(NH_4)_2O + 37Aq.$
$60WO_3.3P_2O_5.2V_2O_5.18BaO + 144Aq.$
$18WO_3.3P_2O_5.4V_2O_5.8K_2O + 32Aq.$
† $7WO_3.P_2O_5.V_2O_5.3K_2O + 11Aq.$

Vanadico-vanadio-molybdates.

$28MoO_3.VO_2.4V_2O_5.11(NH_4)_2O + 20Aq.$
$30MoO_3.3VO_2.2V_2O_5.14BaO + 48Aq.$

Vanadico-vanadio-tungstates.

$12WO_3.3VO_2.2V_2O_5.6Na_2O + 43Aq.$
$12WO_3.3VO_2.2V_2O_5.6(NH_4)_2O + 12Aq.$
$12WO_3.3VO_2.2V_2.2V_2O_5.6Ag_2O + 8Aq.$

Stanno-phospho-molybdates.

$16MoO_3.4SnO_2.3P_2O_5.3(NH_4)_2O + 28Aq.$

Stanno-phospho-tungstates.

$22WO_3.2SnO_2.P_2O_52(NH_4)_2O + 15Aq.$

Phospho-vanadio-vanadico-tungstates.

$60WO_2.3P_2O_5.V_2O_6VO_2.18BaO + 15Aq.$
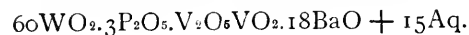
To these I will add the new formulas of the salts described by Struve and Parmentier :

Struve's Salts.
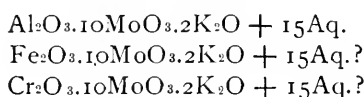
$Al_2O_3.12MO_3.6KO + 20Aq.$
$Al_2O_3.12MoO_3.6(NH_4)_2O + 20Aq.$
$Al_2O_3.12MoO_3.6Na_2O + 22Aq.$[1]
$Fe_2O_3.12MoO_3.6K_2O + 20Aq.$
$Fe_2O_3.12MoO_3.6(NH_4)_2O + 20Aq.$
$Cr_2O_3.12MoO_3.6K_2O + 20Aq.$
$Cr_2O_3.12MoO_3.6(NH_4)_2O + 20Aq.$
$Cr_2O_3.12MoO_3.6Na_2O + 21Aq.$
$Mn_2O_3.16MoO_4.5K_2O + 21Aq.$
$Mn_2O_3.16MoO_3.5(NH_4)_2O + 12Aq.$

Parmentier's Salts.

$Al_2O_3.10MoO_3.2K_2O + 15Aq.$
$Fe_2O_3.10MoO_3.2K_2O + 15Aq.?$
$Cr_2O_3.10MoO_3.2K_2O + 15Aq.?$

[*To be continued.*]

V.—ON THE ESTIMATION OF ACETIC ACID IN LIQUIDS CONTAINING ORGANIC MATTER, BY DISTILLATION.

By H. W. WILEY.

Having had occasion to make an examination of some samples of kumys, I was led to enquire whether any other acid except lactic was present. The microscope showed the presence of bacteria aceti, and thus established the presence of acetic acid.

In a substance so complex as kumys the estimation of a minute quantity of acetic acid is a matter of great difficulty. In order to accomplish it in at least an approximate manner I determined to

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[1] Gentele, Journal für prakt. Chemie, **81**, 413.

try the method of Duclaux[1] which rests upon the assumption that acetic acid in a solution subjected to distillation gives a definite percentage of its weight in given successive portions of the distillate. When ten-elevenths of the original liquid has been distilled the portion of the acid given off amounts to 79.8 per cent.

Mr. A. H. Allen[2] who quotes M. Duclaux' results states that in the only trial he has made of the method, viz.: the estimation of the acid in acetate of lime the quantity obtained was considerably below the amount claimed by M. Duclaux.

This fact caused me to suppose that the actual percentage of acid distilled depended largely on the percentage present as well as on the total amount of the distillate. In order to submit this idea to the test of experiment I made a large number of distillations of pure fresh milk to which varying amounts of acetic acid of known strength were added.

I found that in order to have a liquid residue of 10 to 15 cc. left in the retort when 100 cc. of milk were used and the distillate equalled 100 cc. in volume it was necessary to add to the milk the dilute acid and enough water to bring the total volume up to 130 cc. After numerous trials I find that at least 15 cc. of liquid residue should remain in the retort at the end in order to prevent the casein, sugar, etc., from burning.

The quantity of liquid remaining in the retort was determined by pouring the whole of the residue in a linen filter and measuring the volume of the filtrate. In the following experiments the residual liquid varied between 14 and 16 cc. in quantity. A solution of fifth normal acetic acid was used of which 1 cc. contained .012 gram of pure acid.

Since the amount of acetic acid in sour milk or kumys can never be very great in quantity the trials were made with very weak solutions.

The quantities of fifth normal acid used varied from 5 to 30 cc. in a volume of 130 cc. A large number of distillations were made in various attempts to prevent the frothing of the acidulated milk and the consequent transfer of portions of it to the distillate. The best methods of preventing frothing will be given hereafter.

Method Employed.

In each case 100 cc. of milk were used. To this the acetic acid solution was added and then enough water to make the volume

[1] Ann. Chem. et Phys. (5) Vol. XI, p. 233 *et seq.*
[2] Com. Organic Analysis, 2d edition, Vol, I. p. 408 *et seq.*

up to 130 cc.. Each 10 cc. of the distillate was titrated separately by $\frac{N}{100}$ soda, using phenolphtalein as indicator.

Results with 5 *cc.* $\frac{N}{5}$ HC$_2$H$_3$O$_2$.

Percentage acid present by weight .044. The mean of a large number of distillations showed that the total acid distilled in 100 cc. when the above amount was present was only 7.33 per cent. of the whole. The quantity given off in each 10 cc. of distillate as well as the total is given below:

1.	10 cc. of distillate,		.33 per cent.
2.	10	"	.33– .66
3.	10	"	.39–1.05
4.	10	"	.35–1.40
5.	10	"	.40–1.80
6.	10	"	.59–2.39
7.	10	"	.60–2.99
8.	10	"	.90–3.89
9.	10	"	1.25–5.14
10.	10	"	2.19–7.33

It may be doubted whether it is worth while to try to estimate so minute a portion of acid as .044 per cent., but even this amount can be detected as a trace in a mixture of it with lactic acid, when the latter does not exceed .30 per cent., as will be shown subsequently.

Results with 10 *cc.* $\frac{N}{5}$ HC$_2$H$_3$O$_2$.

10 cc. fifth normal acetic acid contain .12 gram anhydrous acid. In 135 grams this is .089 per cent.

The amount of total acid present coming over with each successive portion of 10 cc. distillate was as follows (mean of 100 tirations):

1.	10 cc.	.89 per cent.
2.	10	1.12– 1.91
3.	10	1.27– 3.18
4.	10	1.31– 4.49
5.	10	1.42– 5.91
6.	10	1.59– 7.50
7.	10	1.87– 9.37
8.	10	2.20–11.57
9.	10	2.69–14.26
10.	10	3.75–18.01

Results with 15 *cc.* $\frac{N}{5}$ $HC_2H_3O_2$.

Following are the mean result of 120 titrations.

Percentage Present.

Fifteen cubic centimetres of fifth normal acetic acid represent a weight of pure acid of .18 gram. In 135 of grams of material this represents .133 per cent.

The mean percentages of total acid present coming over with each successive 10 cc. of distillate were as follows :

1.		10 cc. of distillate.	1.02 per cent.
2.	10	"	1.19– 2.21
3.	10	"	1.28– 3.49
4.	10	"	1.42– 4.91
5.	10	"	1.63– 6.54
6.	10	"	1.97– 8.51
7.	10	"	2.32–10.83
8.	10	"	2.76–13.59
9.	10	"	3.44–17.03
10.	10	"	4.55–21.58

Results with 20 *cc.* $HC_2H_3O_2$.

20 cc. of fifth normal acetic acid have .24 gram of water free acid. In 135 grams of material this amounts to .178 per cent.

In all 260 titrations were made.

Following are the mean results showing percentage of total acid present, coming over in each successive 10 cc. of distillate.

1.	10 cc	1.30 per cent.
2.	10	1.56– 2.86
3.	10	1.78– 4.64
4.	10	1.88– 6.52
5.	10	2.15– 8.67
6.	10	2.50–11.17
7.	10	2.90–14.07
8.	10	3.48–17.55
9.	10	4.23–21.78
10.	10	5.58–27.26

Results with 30 *cc.* $HC_2H_3O_2$.

30 cc. $\frac{N}{5} HC_2H_3O_2$ contain .36 gram anhydrous acid.
In 135 grams of material this is .267 per cent.

The percentage of acid coming over with each successive 10 cc.
distillate was as follows (mean of 120 determinations):

1.	10 cc.	1.80 per cent.
2.	10	1.92– 3.72
3.	10	2.00– 5.72
4.	10	2.13– 7.85
5.	10	2.40–10.25
6.	10	2.75–13.00
7.	10	3.03–16.03
8.	10	3.92–19.75
9.	10	4.80–23.95
10.	10	6.13–30.08

It was reasonable to suppose that an organic acid like lactic acid
would itself be carried over mechanically to a certain extent in the
process of distillation. Since pure acetic acid boils first when the tem-
perature reaches 119°, all that comes over of it also must be carried
mechanically in the other vapors, or as a definite hydrate of low
boiling point. To determine how much of the lactic acid would
thus pass over, a large number of trials were made.   20 cc. $\frac{N}{5}$ lactic
acid in a total weight of 135 grams were used in these determina-
tions. The amount that came over in each successive portion of
10 cc. of distillate was almost constant, and did not rapidly
increase toward the last, as is always the case with acetic acid.
The mean for each 10 cc. was .0064 cc. of the acid employed, or
.0016 per cent. For the whole distillate of 100 cc. this would give
.016 per cent. of the acid present. The percentage of lactic acid
in the mixture distilled was .27. It is fair to presume that with a
larger quantity of lactic acid the amount carried over mechanically
must be somewhat greater.

In any case, however, with small percentage of lactic acid, the
disturbing effect of the quantity going over can be approximately
determined, and in no case is it very great.

It appears, therefore, that in a total acidity (in kumys or sour
milk) of from .50 to 1.00 per cent. due to the two acids, viz. lactic
and acetic, it is possible to determine each of them with a satisfac-

tory degree of accuracy, when the quantity of acetic acid present does not rise above .3 or fall below .1 per cent. If it should be less than .1 per cent. the quantities distilled become so minute that the results are not reliable.

It would be interesting to continue the investigations with larger quantities of both acids, but since they do not usually occur in kumys or sour milk in greater amounts, the operations should be conducted in a liquid of a less complex nature than milk.

Separation of the Two Acids in Artificial Mixtures.

To test the accuracy of the determinations I had my assistant, Mr. Dugan, prepare for me various mixtures of milk and the two acids in proportions unknown to me. In most instances I was able to determine with gratifying accuracy the quantities used. In a few cases, however, the results were not accurate, but these were chiefly due to the use of a smaller quantity of the acids than indicated in the limits stated above, for the accuracy of the method.

Following are some of the results of the separation. The quantities of acid employed as well as of those found by analysis are given in cubic centimetres of fifth normal acid :

Trial No. 1.

Found	...	10.6 cc. acetic acid.
Given	...	10.0 " "
Found	...	00.0 " lactic acid.
Given	...	2.5 " "

Trial No. 2.

Found	...	.92 cc. acetic acid.
Given	...	1.00 " "
Found	...	8.78 " lactic acid.
Given	...	9.00 " "

Trial No. 3.

Found	...	.67 cc. acetic acid.
Given	...	.50 " "
Found	...	8.42 " lactic acid.
Given	...	9.50 " "

Trial No. 4.

Found ... 2.94 cc. acetic acid.
Given ... 3.50 " "
Found ... 6.29 " lactic acid.
Given ... 6.50 " "

Retention of a Portion of the Acid by the Precipitated Casein.

As I have already mentioned, I find that the best method of clarifying the milk for determining total acid present is by mixing it with an equal volume of strong alcohol. I found, however, using known quantities of acid in the milk, in titrating the filtrate, that the total acidity was not indicated. Here are some of the numbers obtained—in parts of acid known to have been added to the milk :

1	94.40 per cent.	(lactic and acetic.)
2	98.04 "	" "
3	86.67 "	(lactic acid alone.)
4	96.20 "	(acetic " ")

It would appear from the above numbers that lactic acid is held back with more tenacity than acetic. As will be seen the error which may occur from the above cause is likely to be greater than that arising from the distillation.

The exact cause of the error, its extent and its remedy are subjects for future study.

As a result of the work the following method of procedure may be recommended :

1. The sample of sour milk is mixed with an equal volume of alcohol, the acid determined in the filtrate with $\frac{N}{5}$ NaOH, using phenolphtalein as indicator. The quantity found to be taken at 95 per cent. of the amount present.

2. 100 cc. of the sour milk are diluted to 130 cc. with water and a distillate of 100 cc. taken off. The acetic acid in this distillate is estimated (using $\frac{N}{50}$ or $\frac{N}{100}$ alkali if necessary).

If less than 12 cc. $\frac{N}{100}$ NaOH are required to neutralise the acid in the distillate, it can be assumed that not more than 10 per cent. of the acetic acid present has been distilled over. From the total acidity, however, must first be deducted that due to the lactic acid carried over mechanically. If .3 per cent. lactic acid be present it will be proper to deduct 6 cc. $\frac{N}{100}$ from the total used.

If 40 cc. $\frac{N}{100}$ be required under the conditions above noted then 18 per cent. of the acetic acid may be considered to have come over. If 70 cc. $\frac{N}{100}$ NaOH be required the acid distilled over should be estimated at 23 per cent.

If 110 $\frac{N}{100}$ NaOH be required, place the amount of acid distilled over at 27 per cent.

If the distillate require 200 cc. $\frac{N}{100}$ NaOH the quantity of acid distilled over can be taken at 31 per cent.

For quantities intermediate among those given allow for proportionate percentages in the distillate.

Frothing of the Sample during Distillation.

Whether the object of distillation be the estimation of acid or alcohol the difficulty of preventing frothing of the sample is great. I found that an ordinary test-tube brush placed in the neck of the flask was a most excellent safety plug. The handle of the brush should be cut off so as not to interfere with the stopper. A thread tied to the stump of the handle and left hanging outside does not interfere with the stopper and is convenient for withdrawing the brush. The brush should be at first pushed into the flask and then by means of the thread pulled up into the throat. The bristles then all point downward in a convenient position to puncture the bubbles. For alcohol distillations nothing better than this need be used. In the case of acids, however, there may be some danger of the metal of the brush being attacked, and some other device must be used. I found a small fine sponge pulled into the throat of the flask by a thread very efficient means of arresting the bubbles. Another excellent device is the use of a plug of fine asbestos fibre or of glass wool. In all these cases the amount of liquid which the plugs will absorb must be approximately known and this additional quantity of water added to the contents of the flask. I also employed a small platinum cylinder punctured with fine holes which was attached by a rubber stopper to the delivery tube. The simplest device of all is to use a flask with a side delivery tube. The neck of the flask should be largest at the top and have a small constriction just as it enters the bulb. A perforated platinum cone large enough to fill the neck is placed point down in it. The constriction prevents it from entering the bulb. In this way the bubbles are prevented from entering the delivery tube and no correction is to be made for absorbed liquids.

VI.—AN EXAMINATION OF WHISKIES.

By Clifford Richardson.

As far as I have been able to learn very few careful examinations of American whiskies are a matter of record. During the past year several samples have come into my hands from reputable retail and wholesale dealers and from bonded warehouses through the United States Commissioner of Internal Revenue. Determinations have been made in these samples of alcohol and solid residue, for the purpose of learning what was to be expected in whiskies of different ages and blendings.

It is well known that a new whiskey contains practically no solids in solution. The amount found after a short time in bonded warehouse is derived from the extractive matter of the wood of the barrels in which the liquor is stored. As the whiskey ages the amount of solid matter it contains increases, both from additional solution and evaporation, or by some of the aging processes which heat the liquor and enable it to dissolve more substances from the staves. After a certain age the " straight whiskies " from the warehouse, on which taxes have been paid, are blended and treated to suit the market. Very few straight whiskies are sold as such in America, it having been found desirable from a commercial point of view to mix the product of different fermentations or mashes which have a different flavor, to add artificial flavoring material, such as tea and spices and sugar, and often to reduce the strength with water.

This is a matter purely of taste. From an analytical point of view, to the food analyst it is of interest to know the limits within which these operations affect the character of a whiskey as manipulated by the best dealers.

The following samples have been examined :

Retail Trade.—3681, Cutter whiskey, eight year old Bourbon, Ky.; 3682, Private Stock, seven year old rye, Pa.; 3683, Loyal Legion, five years old rye, Md.; 3684, Gibson, five year old rye, Pa.; 3685, Orator, five year old rye, Pa.; 3686, Webster, five year old rye; 3687, Cutter D No. 1 five year old rye, Ky.; 3688, XXXX Gibson, four year old rye, Pa.; 3689, Old Crow, five year old Bourbon, Ky.; 3690, Cutter R. R., three year old rye, Ky.; 3691, Hammond, five year old rye, Ohio ; 3692, O. K., four year

old rye, Ky. ; 3693, Stag Head, three year old rye, Ohio ; 3694, Potomac, low grog shop ; 3695, Orator " D," six year old rye, Pa. ; 3696, Orator Cabinet, ? rye, Pa.

From Bonded Warehouse.—1881–9, six samples of different lots about six months old ; 1880–2, three lots of whiskey from Boone Co., Ky., in warehouse but a few months and aged by a patent process ; 3853, Aug. 26, 1885, whiskey from bonded warehouses six months old and dark colored, suspected of being tampered with. 4128, November 26th, 1885 Whiskey, one month old, on sale in Kansas, aged by patent process, Boone County, Mo. The following determinations were made :

EXAMINATION OF WHISKEYS.

Retail and wholesale trade.

No.	Specific Gravity Original Whiskey.	Specific Gravity of Distillate 15° C.	Per cent. of Alcohol.	Total solids per 100.	Ash.
3681	.93692	.93259	43.5	1.0290	.0078
3682	.93662	.93544	42.2	.7176	.0098
3683	.93646	.93396	42.9	.9170	.0060
3684	.93683	.93555	42.1	.5540	.0085
3685	.93470	.93392	42.9	.6168	.0099
3686	.93601	.93488	42.4	.7690	.0110
3687	.93436	.93366	43.0	.5858	.0030
3688	.93602	.93483	42.4	.5902	.0100
3689	.94411	.93835	40.7	1.4520	.0085
3690	.93422	.93335	43.2	.4760	.0039
3691	.93092	.93087	44.4	.1240	.0029
3692	.92894	.92887	45.3	.1500	.0048
3693	.94105	.93746	41.2	.9664	.0039
3694	.95993	.93786	41.0	.2060	.0047
3695	.93650	.93335	43.2	.6964	.0090
3696	.95685	.93445	42.1	.5386	.0078
Average	.93878		42.7	.6493	.0069

Bonded warehouses.

1881	.93418	...	42.8	.0304	...
1882	.93428	...	42.7	.0346	...
1883	.93410	...	42.8	.0304	...
1884	.93337	...	43.2	.0364	...
1885	.93359	...	43.1	.0248	...
1886	.93340	...	43.2	.0396	...
1887	.93292	...	43.4	.0392	...
1889	.93263	...	43.0	.0344	...
Average	.93368	...	43.0	.0337	...

Bonded warehouse; aged by patent process.

No.	Specific Gravity Original Whiskey.	Specific Gravity of Distillate 15° C.	Per cent. of Alcohol.	Total solids per 100.	Ash.
1890	.93502	...	42.4	.0672	...
1891	.93465	...	42.5	.0872	...
1892	.93576	...	42.3	.0500	...
4128	.93620	...	41.6	.0738	.0037
Average	.93841	...	42.4	.0695	...

Bonded warehouse.

3853	.93161	...	44.0	.0616	.0036

The results show at once that a straight whiskey six months old averages only .0337 of solids, while at 4 or 5 years they will not exceed .200, as is shown by the straight whiskies numbered 3691 and 3692. The remaining articles in the retail trade all contain an excess of solids which have evidently been added as flavor. The aging processes, so called, apparently add not nearly so much extractive matter to the liquor as one might expect and in no way conceals the true character, although perhaps volatilising a little alcohol and rendering it weaker. In the 29 samples examined the percentage of alcohol varied within rather narrow limits, but one having above 44 per cent., three above 43 per cent., and but three below 42 per cent., twenty-two contain from 42 to 43 per cent. of alcohol by weight, and as the " Proof Spirit " of the United States contains 42.7 per cent. by weight of alcohol, the samples all varied very little from proof.

It will be seen that the evidence of these determinations is sufficient, at least to show whether a whiskey is a straight article or has been flavored.

WASHINGTON, D. C., *November 26th*, 1885.

NOTES.

On "*Explosive Ice.*"

During the very cold weather of the week January 8th to 15th, a French "*gazogène*" or portable apparatus for preparing carbonic-acid water under pressure was destroyed in the laboratory of the University of Virginia, by the freezing of the contents of the upper globe, which was almost completely full of distilled water charged with carbonic acid, and was burst by the expansion of the ice formed. The globe, which was surrounded by basket-work of split cane, was of heavy glass, about 8 mm. in thickness, and must have burst with some violence, judging from the distance to which the disc-like top was thrown. Having removed the apparatus to a warm room, in which thawing might take place without the liquid running about on the shelves and floor of the apparatus room, I had my attention attracted in a few minutes by little crackling explosions coming from the ice, which, when brought in, was quite solid and dry—much below the melting-point. Standing near and somewhat above the level of the apparatus, which had been placed in one of the laboratory sinks, I was two or three times struck in the face by little bits of ice as large as hazel-nuts, thrown off with some force from the bulk of the frozen mass. One piece, fully as large as a walnut, was thrown off to a distance of seven or eight feet upon the floor. Some of the crackling sounds fairly merited the name of explosions. Once or twice the sound was quite as loud as that produced by suddenly treading upon a friction-match.

The ice was in the main white and translucent, but with many small, glassy streaks of complete transparency running through it. It obviously contained a multitude of pretty uniformly distributed, minute bubbles of carbon-dioxide gas, under heavy pressure—pressure not due merely to the space within which the gas had been originally generated, but greatly increased by the expansion of the water in the act of freezing as the gas separated out from it. It is, perhaps, not impossible that, at the existing temperature, this pressure may have even sufficed to liquefy some of the gas of the bubbles caught in the interior of the ice. The immediate cause of the explosive splitting up of the ice under the tension of the included carbon dioxide seemed to be the weakening of the forms by expansion in the comparatively warm atmosphere of the room : there was but little melting during the time, some three-quarters of an hour, during which the crackling sounds and the flying to pieces of the ice lasted. A little explosion could easily be induced by striking a very slight blow with a little blowpipe hammer, or with a chisel or other sharp-pointed tool, on almost any part of the ice which had not

before been so treated, and on breaking off some large pieces of the ice and placing them on the table, detached from the rest of the mass, they continued to split and fly to pieces in a very remarkable way.

The whole of the phenomena reproduced exactly the behavior of the quartz from Branchville in Connecticut, in which occur numerous microscopic cavities containing partly liquefied carbon dioxide; but in the case now described, the explosive splitting up by heating was produced at a much lower point on the thermometric scale.

J. W. MALLET.

UNIVERSITY OF VIRGINIA, *January* 18, 1886.

A Gas-Absorption and Measuring Tube.

The accompanying figure, which requires little explanation, represents a form of nitrometer and gas-absorption apparatus that I have found convenient. The measuring tube is graduated in both directions from the stop-cock in cubic centimetres and fractions. The pressure tube is adapted by a ground-joint, and both pressure tube and measuring tube are correspondingly graduated in millimetres. The divisions and their numbers being the same, when the apparatus stands on a level surface the use of a cathetometer is unnecessary.

The stop-cock may be three-wayed, as in Lunge's nitrometer, and the gas can then be transferred to another similar tube when incompatible absorbents are to be employed.

WM. H. GREENE, M. D.

CENTRAL HIGH SCHOOL, *Philadelphia, Nov.* 15, 1885.

Wöhler Monument.

A committee has recently been organised in this country for the purpose of securing subscriptions to the Wöhler-monument fund. According to the last report from Germany, the fund had reached the sum of about $4000. Much more is needed. The chemists of America owe more to Wöhler than to any other one man, and it is hoped that a generous response will be made to the circular which has been sent out by the committee.

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F. W. C.

ERRATA.

Page 349 (Vol. 7, No. 5). Fourth line in paragraph 1. *For* 'is found'
read 'is not found'; and after filtrate *for* the rest of the paragraph *read* 'for
the central part of the exceedingly minute grains even of the ore is still
magnetic; it has escaped oxidation, and, in consequence of this, it retains
some vanadium.'

Page 353. Fourth line in paragraph 19. *For* 'if there is a remnant'
read 'with the remnant.'

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